MPHIL

Process Improvements for the Manufacture of Industrial Polymeric Filters

Kurup, Sreeni

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PROCESS IMPROVEMENTS FOR THE MANUFACTURE OF INDUSTRIAL POLYMERIC FILTERS

SREENI KURUP

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IV. ACKNOWLEDGEMENTS

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V. ABSTRACT

This thesis examines the work that was carried over a period of 24 months within a Knowledge Transfer Partnership (KTP) between the University of Bath and Pall Europe, Ilfracombe. Materials technology expertise has enabled improvements in processing and enhanced quality control in a polymeric filter manufacturing plant. Manufacturing costs within the UK are increasing much faster than other manufacturing locations worldwide. New manufacturing strategies and the introduction of new technologies are required to make further step changes in competitiveness. The partnership has underpinned the successful introduction of a new quality assessment and evaluation method using identiPol-QA for final approval of manufactured products. A benchmark has been created for each grade of polymer and a quality control procedure has been established on the premises of three suppliers who manufacture moulded components for Pall Ilfracombe. The program of work constitutes a series of projects for better control of materials processing, improvement in production performance and best use of materials for new product developments. The thesis details the assessment that has been carried out to understand the level of materials related problems that are occurring across the whole Ilfracombe site. The thesis describes steps taken to investigate the root cause of the materials related processing issues and proposes superior methods for streamlining production within the factory. The work also details the success of the establishment of an advanced materials characterisation facility within Pall Ilfracombe and the impact it has created in the manufacture and research and development of Pall products. In addition, this thesis details various aspects of the importance of the Six Sigma methodology for process improvements in manufacturing filters. Finally the thesis is concluded by detailing the opportunities for future work arising from this study.

VI. GLOSSARY OF TERMS AND ABBREVIATIONS

CAPEX: Capital Expenditure

CTQ: Critical to Quality

DMAIC: Define, Measure, Analyse, Improve and Control

DMTA: Dynamic Mechanical Thermal Analyser

DSC: Differential Scanning Calorimetry

FTIR: Fourier Transform Infrared Spectroscopy

GPC: Gel Permeation Chromatography

HSM: Hot Stage Microscope

IR: InfraRed

KTP: Knowledge Transfer Partnership

PBT: Polybutylene Terepthalate

PCA: Principal Component Analysis

PET: Polyethylene Terepthalate

PILF: Pall Ilfracombe

PLC: Programmable Logic Controller

PP: Polypropylene

PPM: Parts Per Million

PSS: Porous Stainless Steel

QC: Quality Control

QIS: Quality Index Score

S&P: Standard and Poor's

SLS: Scientific and Laboratory Services

TGA: Thermogravimetric Analysis

Tg: Glass Transition Temperature

Tm: Melting Temperature

Tc: Crystallisation Temperature

VOC: Voice of the Customer

CHAPTER 1. INTRODUCTION

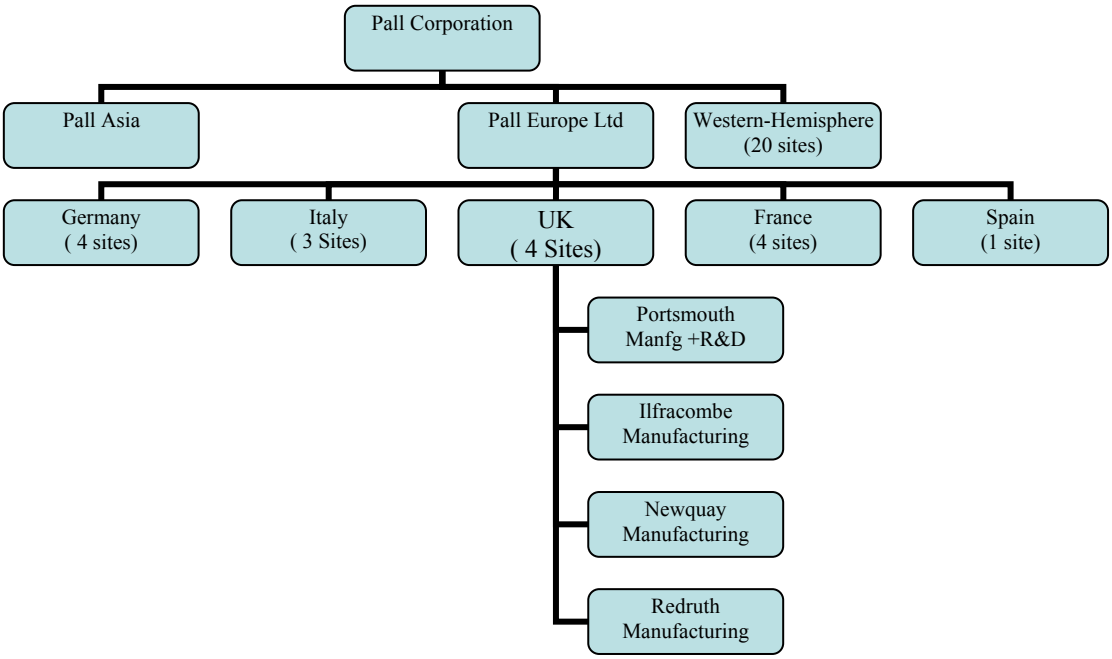
1.1. BACKGROUND

Pall Corporation is recognised as the world leader in filtration separation technology. Pall Corporation is an international company with world class technical excellence and manufacturing capability all around the world. Pall Ilfracombe was established in 1979 and specialises in manufacturing products for life science and industrial application. The company has three other manufacturing operations in the UK and most of the research and development works are carried out at the Portsmouth, Walton Street facility. Pall Ilfracombe is one of a number of manufacturing businesses within Pall Europe Ltd and is a supplier for the global business of pharmaceutical and industrial filter products. Table 1.1 shows the structure of Pall Corporation. Most of the filters manufactured in Pall Ilfracombe are polymer-based and a Knowledge Transfer Partnership (KTP) was established to transfer polymeric materials expertise to the company to enable process improvements in manufacture and to increase the quality of existing and new products. Pall's global markets are classified into four categories

1) Medical
2) Biopharmaceuticals
3) Fluid processing and
4) Aeropower

Pall's products are widely used in medical applications to remove unwanted components from the blood and to reduce transfusion complications. Pall's products are very common in the life science and industrial sectors to filter water, biological products, fuels and chemicals (Pall Corporation, 2010). Other filters include breathing systems developed by Pall, which can remove bacteria and viruses and these filters are very common in medical industries. The aerospace industry depends on Pall's technology to remove contaminants from fuel, hydraulics and lubricating fluids. So basically Pall's products help many industries to satisfy their requirements for filtration.

Table 1.1. Organisational diagram of Pall Corporation



1.2. AIM AND OBJECTIVES OF THE THESIS

Pall Corporation is a materials science specialised company with wide range of filtration separation and purification products. Developing new technologies and introducing new products in the market are very essential in the current economic circumstances for a step change in competitiveness. The aim of this project was to introduce a strategy for the process improvements for the manufacture of industrial polymeric filters and following are the five clear objectives set at the beginning of the work to achieve the project goal.

i. Transfer polymeric materials knowledge to the company for the development of new products through effective materials selection and quality evaluation

ii. Set up a materials characterisation facility at Pall Ilfracombe to assure the quality of plastic parts used to manufacture filter modules

iii. Provide, via onsite materials characterisation, a better understanding of the materials and creates a general awareness of material's physical, chemical and thermal behaviour.

iv. Evaluate production line issues and through the understanding of the materials chemistry to optimise processing parameters.

v. Implement and demonstrate Six Sigma process improvement approaches for quality control of materials.

1.3. LAYOUT OF REPORT

This report starts in chapter 2 with a brief introduction about Pall Corporation and the filtration industry. Processing related issues and thermal degradation mechanisms of polymers are covered in chapter 3. This chapter also covers quality assessments and quality control methods in plastic processing industries. Degradation mechanism of virgin and recycled polymers are different and the applications where recycled polymers cannot be used for making products at Pall Ilfracombe are discussed in this chapter. Various characterisation methods used for polymer analysis are specified in chapter 4. The application of these methods to characterise polymeric materials and the assessment of materials related manufacturing issues are the key focus of this chapter. Establishment of an advanced materials characterisation facility was one of the many achievements within this KTP program. Chapter 5 of this thesis covers various polymer characterisation techniques and their application within Pall Ilfracombe for the selection and quality assessment of materials to manufacture best quality filter systems. Several case studies including identification of batch to batch variation in polymer feed stock, investigation on contamination issues, welding / endcapping issues are explained in this thesis with relevant examples. Chapter 6 covers the implementation of a quality control procedure using thermal analysis equipment (identiPol-QA) within Pall Ilfracome to identify batch to batch variations in polymer feedstock. Chapter 7

explains the importance of LEAN/SIX Sigma methodology for process excellence and its application for optimisation of non contact weld parameters for welding filter components. All of the threads of the thesis are drawn together in a general discussion and conclusions (chapter 8) and the opportunities for future work are discussed in the final chapter 9.

CHAPTER 2. COMPANY AND PRODUCT PROFILE

2.1. PALL CORPORATION

Pall Corporation was founded in 1946 to commercialise Dr. Pall's first invention, a novel metallic filtration material comprising a sintered metal powder as the medium for a porous stainless steel filter (PSS). In the early 1950's Dr. Pall developed an original woven metal mesh that prevented the hydraulic systems of commercial jets from jamming. This was a key development for Pall and establishing Pall Corporation as the aerospace industry's leading filtration supplier. Today Pall Corporation is an established company with world class filtration solutions and provides filters to a wide range of industries.

Pall Corporation, with total revenues of $2.3 billion for fiscal year 2009, is a Standard and Poor's (S&P) 500 company with more than 10,000 employees servicing customers worldwide (Figure 2.1, Pall 2009).

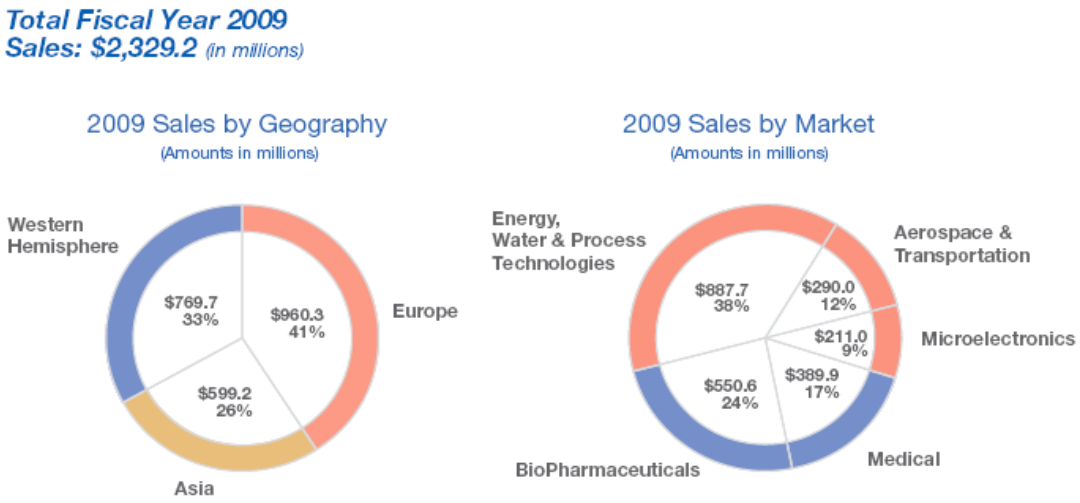


Figure 2.1 Total Fiscal Year 2009 Sales (From Pall Fact Sheet 10/19/09 Page 2)

Pall's influence as the leader in filtration technology has spread exponentially over the last few decades. Pall's products are successfully used in aerospace and transportation, energy, water, microelectronics, food and beverage and environmental science industries. In 1970's, Pall's entry into biopharmaceuticals and medicine with fine and ultrafine disposable filters secured a strong position for the future of the company's contamination management and purification products. Strong competition exists within the market and there are several global competitors with similar product ranges e.g.: Millipore, Sartorius, Dominic Hunter, Cuno. Competition is strong in all areas of the market but no other companies cover the full range of products to the extent of Pall Corporation (Brailey, 2009)

The headquarters of Pall Corporation is in Port Washington, New York and there are extensive operations around the world. Pall Corporation's major research and development work is carried out in the USA. Pall Europe's R&D work is carried out at the Portsmouth, Walton Road site however this is mainly focused on new product design. Pall's Scientific and Laboratory Services (SLS) comprises thirty five laboratory facilities at strategic locations world-wide. Many of these laboratories have advanced testing equipment to test Pall's products. This laboratory network is backed by specific centres of expertise in manufacturing and has direct access to core Research and Development centres.

Biotechnology products and processes are meeting more demanding specifications and Pall's research and development units have specialised biological laboratories to develop new products to support customers (Pall Biopharm. 2009). In response to the increasing importance of biotechnology processes and products, specialised biology laboratories have been created in Portsmouth (UK) and in Florida and New York (USA).

Pall's products can be classified into two major categories: Industrial products and Life science products. Industrial products includes Aerospace/defence/marine, food and beverage, fuels and chemicals, micro electronics, power generation etc and life

science products include biopharmaceuticals, laboratory, medical etc. Figure 2.2 classifies Pall's filtration products based on various applications.

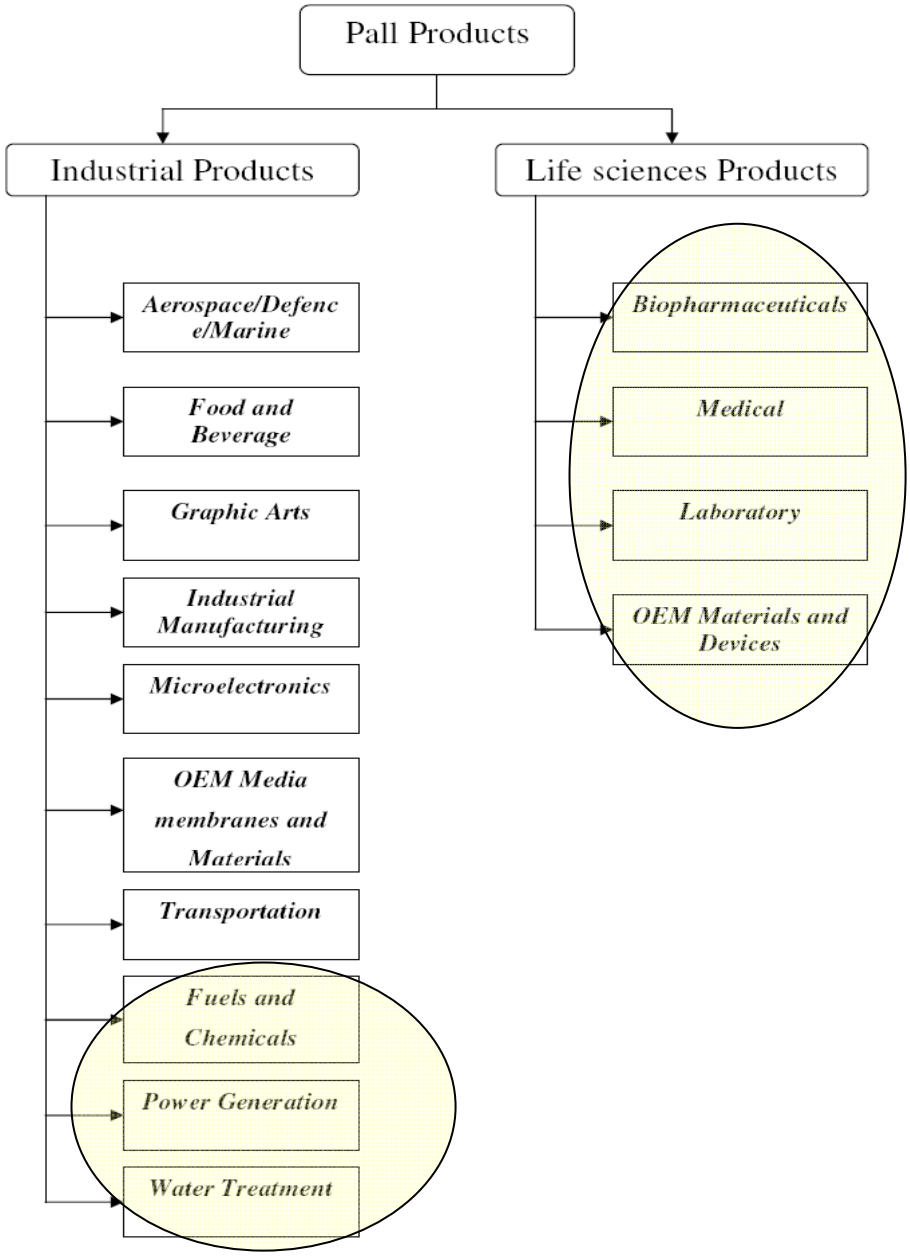


Figure 2.2 Classification of Pall's products- Pall Ilfracombe manufactures the highlighted products

2.2. FILTER TECHNOLOGY

Filtration is the process of removing solid particles from a liquid or gas by passing it through a permeable medium. There are three mechanisms for the separation of solids from liquid or gas; a) Inertial impaction b) Diffusion interception and c) Direct interception.

a) Internal impaction

In this process when the liquid and entrained particles pass through the filter media, the solid particles located at or near the flow line impact on the filter medium and are removed. Figure 2.3 is a schematic representation of internal impaction.

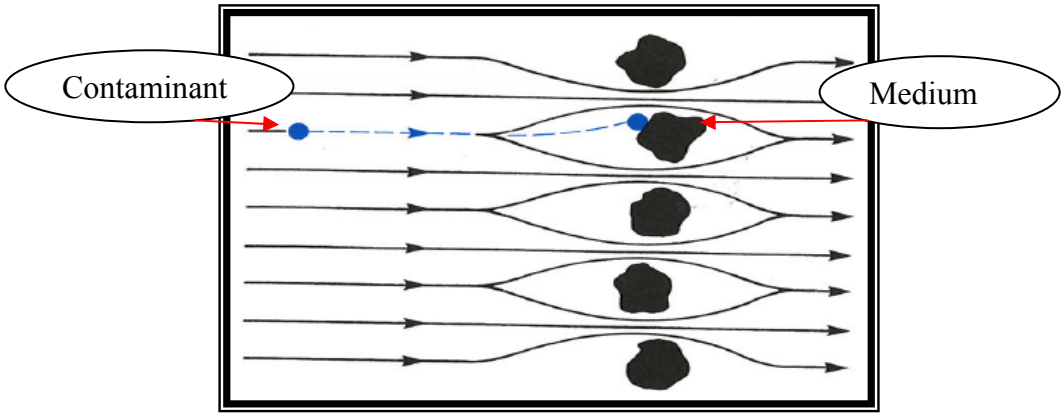


Figure 2.3- Internal Impaction. {Taken from Scientific and Technical Report, Pall Corporation (Principles of Filtration) 1998}

b) Diffusional interception

In this process the particles with extremely small mass are in collision with the liquid molecules and cause the particles to move in Brownian motion. This motion causes the small particles to deviate from the fluid flow lines and hence increase the chance of impact on the polymeric micro porous membrane and removal. This

process has only a minor role in liquid filtration but is highly significant in gases. Figure 2.4 is a schematic representation of diffusional interception.

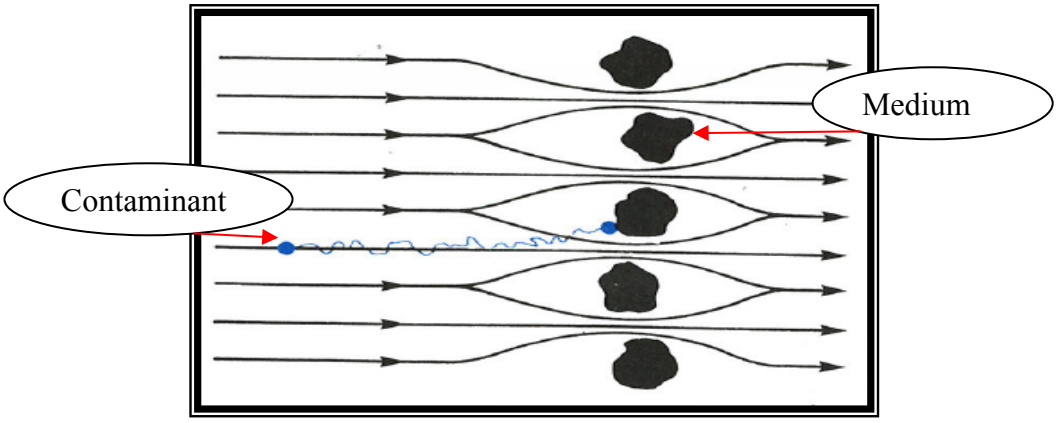


Figure 2.4 Diffusional interception {Taken from Scientific and Technical Report, Pall Corporation (Principles of Filtration) 1998}

c) Direct interception

If the particles within the liquid medium are larger than the pores in the filter medium, they will be removed as a result of direct interception by the holes. This process is effective in the filtration of both liquid and gas. Figure 2.5 is a schematic representation of diffusional interception.

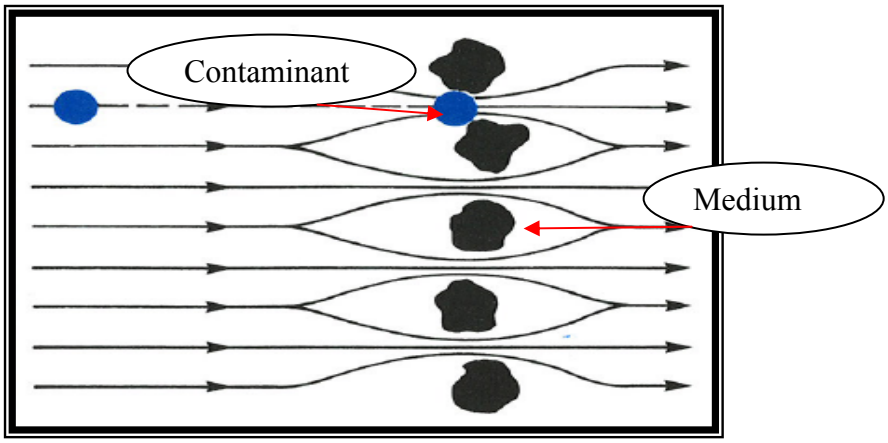


Figure 2.5 Direct interception {Taken from Scientific and Technical Report, Pall Corporation (Principles of Filtration) 1998}

2.3 MANUFACTURE OF INDUSTRIAL FILTERS

2.3.1 THERMOPLASTICS FOR MOULDED PRODUCTS

The word polymer originates from the Greek words ‘poly’ meaning many and ‘mer’ meaning part. Within the polymer the constitutional repeating units and the atoms of the repeating units are linked by covalent bonds. A monomer is the substance that the polymer is made from and the process that converts a monomer to a polymer is called polymerisation. Polymers can be divided into two main classes: Fully amorphous polymers and semicrystalline polymers. Fully amorphous polymers do not crystallise and the reason why these polymers are unable to crystallize is because of their irregular chain structure. For semicrystalline polymers the degree of crystallinity can be as high as 90% for low molecular weight polyethylenes and as low as 5% for polyvinyl chlorides (*Gedde, 1995*).

Polymers can be subdivided into three main categories; ***Thermoplastics*** consists of individual long chain molecules which can be reprocessed by using an appropriate machine; ***Thermosets*** contain an infinite three dimensional networks which is only created when the product is in its final form and cannot be broken down by reheating. The third category is called ***rubber*** which contains looser three dimensional networks, where the chains are free to change their shapes but with some constraints due to the presence of crosslinks (Mills, 1986). A filter module is composed of a filter media, core, cage and end cap. All these components are made of polymers. Based on the application, different polymers are chosen for making each component. Core, cage and end caps are manufactured using injection moulding process. All the above components are assembled together using various plastics welding techniques to manufacture the filter module.

2.3.2. INJECTION MOULDING PROCESS

Injection moulding is the most important plastic manufacturing process used to

produce large quantities of identical plastic parts. It is a manufacturing process which can be used for moulding both thermoplastics and thermosets. The injection moulding process involves the injection of a polymer melt into a mold where the melt cools and solidifies to form a plastic product. Moulding is generally a three phase process comprising filling, packing and cooling phases *(Seow and Lam, 1996)*.

Advantages of injection molding are high production rates, repeatable high tolerances, the ability to use a wide range of materials, low labour cost, minimal scrap losses and little need to finish parts after molding. Some disadvantages of this process are expensive equipment investment, potentially high running costs, and the need to design moldable parts. Figure 2.6 shows the schematics of an injection moulding process.

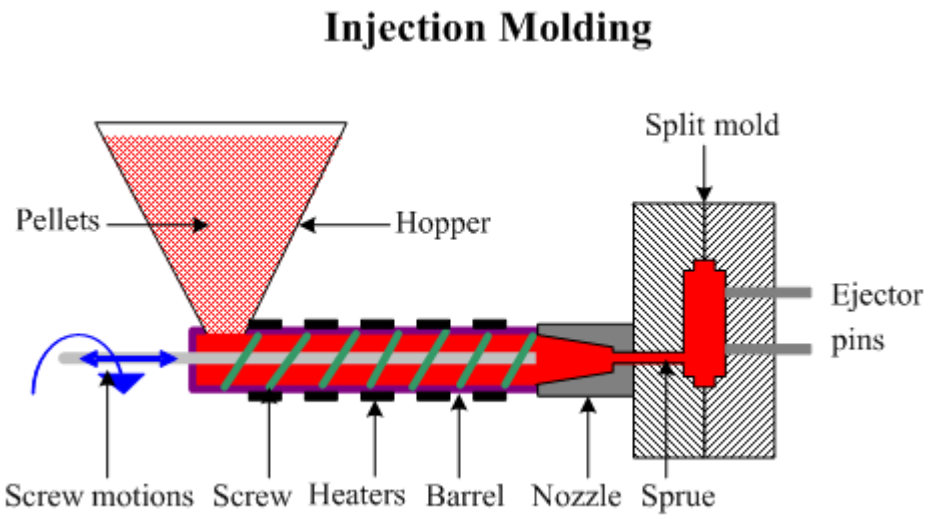


Figure 2.6: Schematic representation of injection moulding process {Adapted from www.substech.com , 2012}

Injection moulding machine consists of a screw-barrel assembly, heater bands and mould tool. During injection moulding process, granular plastic is fed by gravity from a hopper into a pre-heated barrel. The granules are slowly pushed forward by a

screw-type plunger. This plastic is forced into a heated chamber where the plastic granules are converted to molten plastic. As the plunger advances, the melted plastic is forced through a nozzle that rests against the mold, allowing it to enter the mold cavity through a gate and runner system. The mold remains cold so the plastic solidifies almost as soon as the mold is filled. Pall subcontracts for the manufacture of most of the injection moulded parts. Figure 2.6 shows various injection moulded components and corrugated media used for manufacturing the filter module**.**

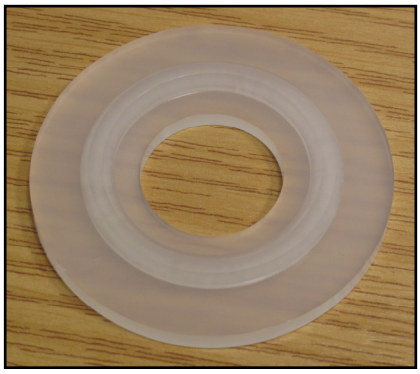
The filter media is the key element of the filter module. The filter media is classified into two types:

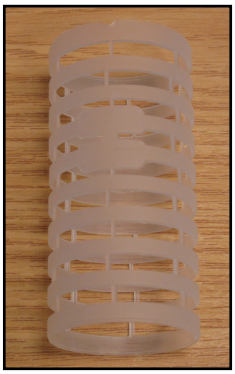
a) Non fixed pore filter media in which the dimensions of the pores increase at high pressure. Examples of these types of filters are woven yarns, loosely packed fibreglass and asbestos pads

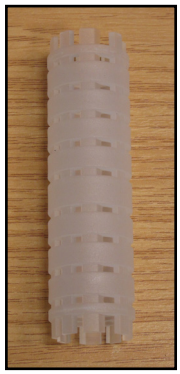
b) Fixed pore filter media, in which the pore size is fixed and does not increase or decrease in size at high pressure.

This type of filters uses the direct interception mechanism. The fixed pore filter is better for most applications and these filters can retain some particles by adsorption as a result of inertial impaction and diffusional interception (Principles of Filtration, 1998).

End cap ***Cage*** ***Core***







Bombfin ***Adaptor***

Corrugated media

Figure 2.7: Injection moulded components and corrugated media for manufacturing filter modules

2.3.3 END-CAPPING PROCESS

End-capping is the process of attaching the endcaps on both sides of the assembled module and this is one of the key processes in manufacturing filter modules. The selection of endcaps depends on the application of the product. The end-capping processing parameters are carefully optimised for each material to achieve the best performance. During the end-capping process the surface of the end-cap is melted using a non-contact heater plate. The melted end-cap is brought into contact with the module assembly and force is applied to achieve the best melt penetration. It is extremely important to make sure that all the end-capped filters meet the specified quality requirements. Most likely faults after the end-capping process are:

- Flash (Excess material generated by the process)
- Over melt (Platen temperature too high)
- Cage and core engagement (misalignment of components)
- Misalignment of endcaps (endcaps should be square to and aligned with the body of the filter)
- Discolouration (mainly due to thermal degradation)
- Pleat bend (poor corrugation or excess pressure applied to media)
- Inclusions (a hair, fibre or other particle trapped but visible within the plastic).
- Dirty marks (due to handling)
- Voids or bubbles (entrapment of air during processing)

The KTP program was initiated to solve problems associated with the manufacture of filter assemblies, many of which are included in the list above. Furthermore quality assurance techniques were required to confirm the consistent quality of polymer feedstock supplied to moulders.

2.3.4 PLASTIC WELDING

Plastic parts can be joining together by mechanical fastening, adhesive joints or

plastic welding. Mechanical fasteners can join two components quickly, but they do not provide a leak tight joint, and the localized stresses may cause them to pull free of the polymeric material. Adhesives can provide good joints, but they are difficult to handle and takes more time cure (Uday *et al*, 2010). Welding can be used to produce bonded joints with mechanical properties that are nearly the same as the parent material. Plastic welding can only be used for joining thermoplastic components. Thermosetting polymers once hardened cannot be softened again on heating. There are different techniques to weld thermoplastics and most common methods use at Pall Ilfracombe are ultrasonic welding, induction welding, friction welding, hot plate welding, hot gas welding, spin welding and IR welding.

Figure 2.8 explains the manufacturing process for making filter modules. Filter manufacturing process involves nine different stages and all these stages are very critical for the manufacturing of best quality filters. Functions of each stage are briefly explained in the picture below.

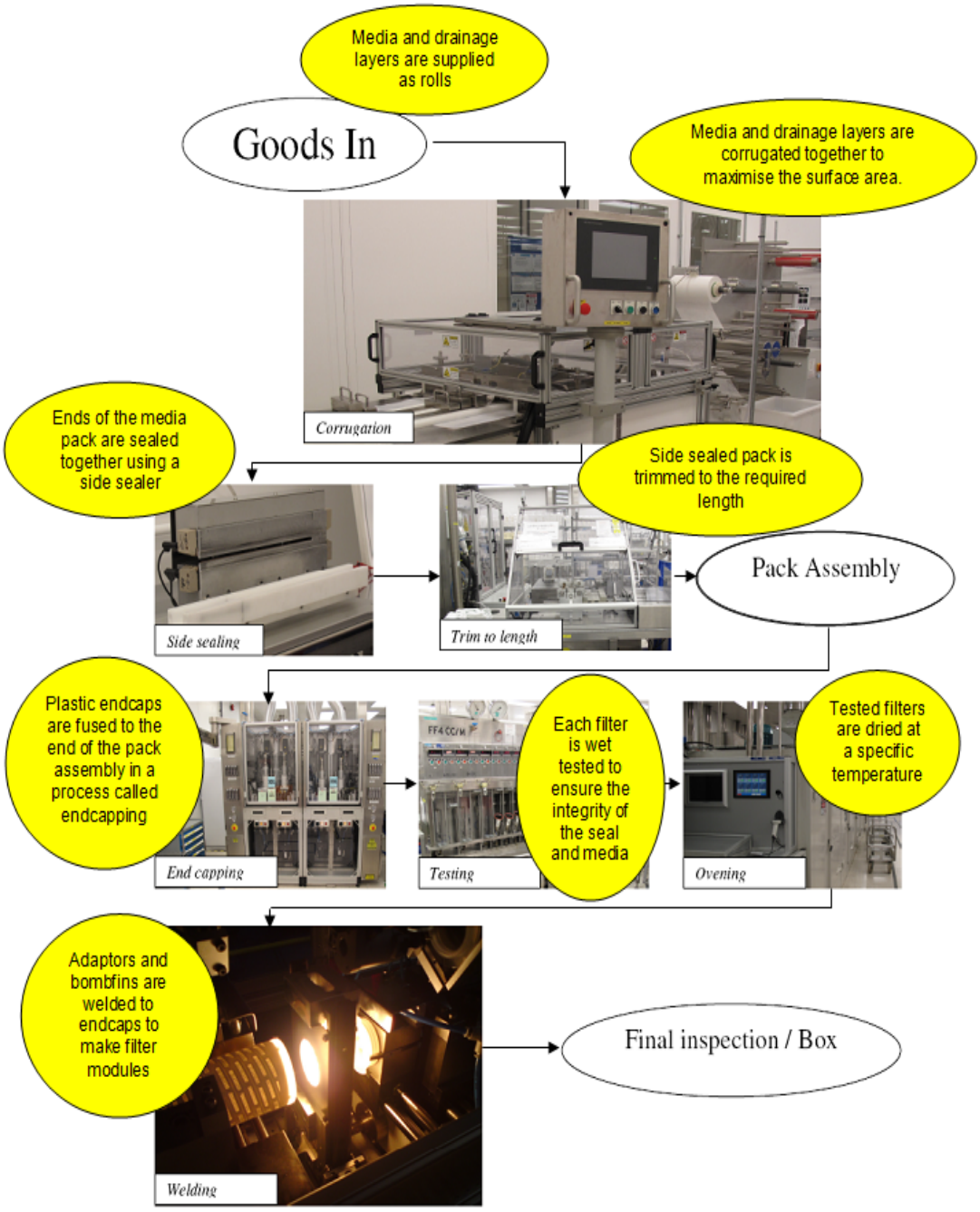


Figure 2.8: Filter manufacturing process

2.4. CHAPTER SUMMARY

This chapter has provided an overview on Pall Corporation and Pall's influence as a leader in filtration technology. The headquarters of Pall Corporation is in Port Washington, New York and major R&D works are carried out at the Portsmouth, Walton Road site, UK. Pall's products are classified into two major categories: Industrial products and Life science products. Classification of Pall's products based on various filtration applications and the three different mechanisms of filtration technology was briefly covered in this chapter. Explanation of different processes involved in the manufacture of industrial polymeric filters was the main focus of this chapter.

CHAPTER 3. LITERATURE REVIEW- QUALITY ISSUES IN POLYMER PROCESSING

3.1. INTRODUCTION

Main causes of polymer processing issue are due to the high melt viscosity of the polymer. Selection of higher processing temperature can reduce the melt viscosity but most polymers are thermally unstable and cause thermal degradation. Colin and Verdu (2006) have explained how polymers properties changes with processing temperature. At low temperature the thermal degradation is very minimal but the effect of physical properties like high melt viscosity on product quality is high. But as the temperature increases the melt viscosity decreases and the part quality is limited by thermal aging. In the contest of Pall Europe, injection moulding and end-capping are the processes where thermal degradation may cause failure of filter assemblies. As discussed in chapter 2 of this thesis, Pall's products are classified into two major categories: industrial products and life science products. In response to the increasing quality requirements for the life science products, specialised clean room manufacturing process have been created at Pall Europe where all the filter components are manufactured using virgin polymers. Quality issues such as thermal degradation during processing of virgin and recycled polymers, contamination issues and batch to batch variation in polymer feed stock are some of the particular issues most relevant to filter manufacture at Pall Europe. This chapter provides a comprehensive review on some of the key quality issues in polymeric filter manufacturing at Pall Europe and the importance of implementing quality assessments and quality control methods to solve processing related issues.

3.2. THERMAL DEGRADATION IN POLYOLEFINS AND THEIR BLENDS

Research on the thermo-oxidative and thermo mechanical stability of polyolefins has

been extensively reported in the literature. Polyolefins, mainly polypropylenes are widely used in the manufacture of polymeric filter modules. Polypropylene is classified as semi-crystalline polymer and this material has melting point occurs as range. This makes polypropylene easy for processing without changing its physical properties compared to other semi crystalline polymers. Polypropylene is tough and flexible and has good chemical resistance to consider this material for making cores, cages and end caps of filter modules. The temperature and high shear force employed during polypropylene processing can cause chemical changes within the material and a small change in chemical reaction can enormously change the physical properties of the polymer (Hinsken *et al*. 1991). In many cases degradation is initiated by oxidation, shear heat, catalystic reaction or a combination of these factors. Thermal oxidation of polypropylene results in chain scission and reduction in mechanical properties such as toughness and flexibility. Selection of suitable grades of material and processing conditions are critical to maintain the physical properties of polymers after processing.

Polymer blends are often considered for filtration applications to meet specific property requirements. There are only limited data published on degradation mechanism of polymer blends such as polypropylene impact copolymers during processing (Tochacek *et al*. 2006). Polypropylene impact copolymer is a blend of polypropylene, polyethylene and small portion of ethylene-propylene rubber. An attempt to investigate the degradation process taking place in polypropylene impact copolymers during processing was explained and published by Tochacek *et al,* (2008). It was concluded that the polypropylene impact copolymer behaved in a similar way to polypropylene because the polypropylene constitutes the majority of the mass of the polymer. Also it was concluded that the degradation taking place in the rubbery phase might not affect the over all behaviour of the polymer.

General aspects of polymers and polymer blend degradation has been studied and discussed by Pospisil *et al*, (1999). Difference in sensitivity to individual degradation process during polymer processing happens due to the inhomogeneity of

the polymer blend and the presence of non polymeric additives. Therefore in many cases the degradation behaviour of polymer blend is difficult to predict without experiments.

Thermo-mechanical degradation of polymers happens when polymers are melt processed at elevated temperature in a low oxygen atmosphere. Non reactive polymers such as polyolefins undergo thermo-mechanical degradation in a range of temperatures where they are practically unaffected by thermal treatment alone. But Pospisil *et al,* (1999) has described that under industrial processing conditions, traces of oxygen were presented in the mixing equipment and this caused thermo-oxidative degradation of the polymers during processing. Goldberg & Zaikov (1987) studied the kinetics of mechanical degradation of polymer melts during processing. During melt processing polymers undergo mechanical degradation and thermo oxidative degradation. Both degradation mechanisms were studied in detail and published in many papers. During mechanical degradation free radicals are formed when polymer chains are broken. These free radicals ($R^{\bullet}$) decay at the same rate as chain scission and thereby decrease the molecular weight. Therefore in the majority of cases molecular weight decreases during mechanical degradation. Goldberg & Zaikov (1987) have reported that thermal oxidation can influence molecular weight by the formation of crosslinks due to the combination of free radicals, $R^{\bullet}$ or $RO^{\bullet}$ and if the concentration of oxygen is high then all the alkyl ($R^{\bullet}$) is converted into peroxide ($RO^{\bullet}_2$). Therefore during thermal oxidation, the following reaction happens

$$R^{\bullet} + O_2 \longrightarrow RO^{\bullet}_2 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (1)$$

$$RO^{\bullet}_2 + RH \longrightarrow R^{\bullet} + ROOH \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (2)$$

Figure 3.1 is a kinetic model which shows reactions for thermal degradation and thermo oxidative degradation during polymer melt processing. This model include reactions for changes in molecular weight during processing and these are oxidative scission, mechanically activated crosslinking and mechanically activated scission.

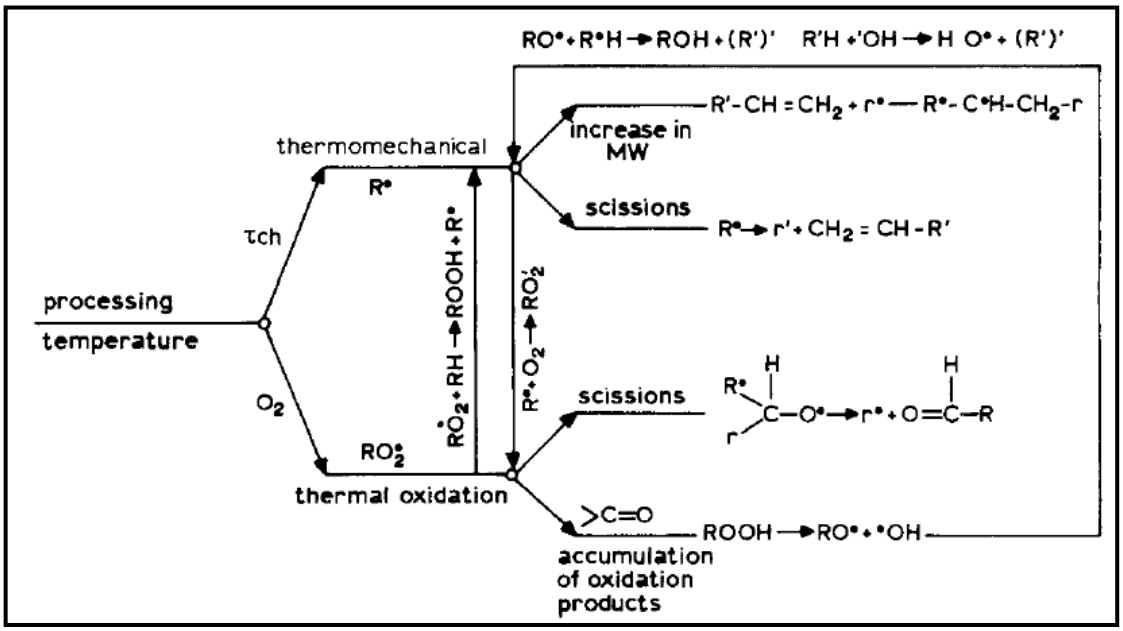


Figure 3.1 - Change in molecular structure due to thermal degradation and thermo oxidative degradation during polymer melt processing {Goldberg & Zaikov, 1987}

3.3. THERMAL DEGRADATION IN POLYESTERS

Due to unique chemical characteristics and mechanical properties, polyesters are widely used in filter modules and filter media manufacturing. Polyethylene terephthalate (PET) and polybutylene terephthalate (PBT) are the two types of polyesters used in Pall Europe for making filter media and end-caps. Compared to polyolefins, the degradations mechanism of polyesters during processing are different and have received continuing attention in many literatures. Samperi *et al,* (2004) has studied the isothermal degradation of PET in the temperature range of 270 to 370°C. Mass spectroscopy and NMR analysis were conducted to study the structural change due to thermal degradation. Formation of acetaldehyde in the PET samples and the formation of hydrolytic reaction in PET when the material comes in contact with water at elevated temperature were clearly explained. Figure 3.2 shows the change in molecular weight of PET at 285°C with and with out the addition of 0.5% p-TsOH.H_2O. The molecular weight of pure PET remains unaltered whereas

the presence of *p*-TsOH.H_2O has dramatically decreased the molecular weight of PET at 285°C due to strong hydrolytic reaction with consequent increase of carboxyl terminated polyester chains.

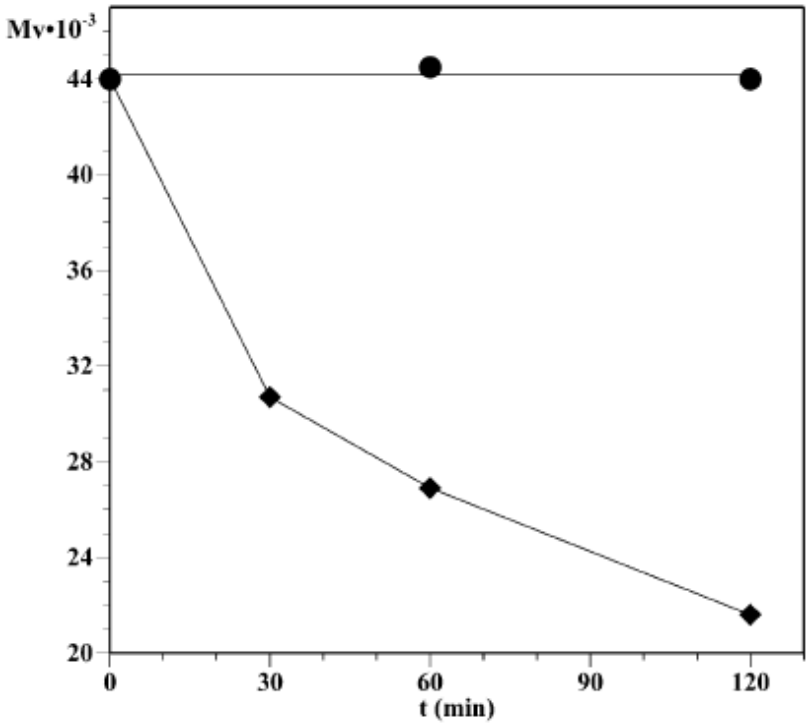


Figure 3.2 Molecular weight Vs Heating time for PET at 285°C with (♦) and with out (●) the presence of p-TsOH.H_2O { Samperi et al, 2004}

Samperi *et al*, 2003 explained the isothermal degradation mechanism of PBT in the temperature range of 270 to 350°C. Results show although the aromatic polyester structures are quite similar in both PET and PBT, the butylene group in PBT is able to create significant degradation in PBT compared to PET. It is concluded that the different thermal degradation behaviour observed in PET and PBT is due to the difference in reactivity of ethylene and butylene groups and also due to higher chain flexibility of the PBT chains with respect to PET.

3.4. DEGRADATION IN RECYCLED POLYMERS

Degradation mechanisms of reprocessed polymers are a hot topic in today's research. The usage of commodity polymers has been increased worldwide and hence recycling of polymers has significant environmental benefits. Recycling of thermoplastics can be done using standard processing equipment but there is always a risk of contamination of recycled polymers compared to virgin polymers. Recycling is environmentally friendly and also economically advantageous but there are applications where recycled materials cannot be used for making products due to quality concerns and this includes biomedical products such as polymeric filters.

Recently the degradation mechanisms of polyethylene during reprocessing has been studied and published by Bernardo *et al*, (2011). Polyethylene is one of the most consumed commodity plastic and significant amount of research has been devoted to understand the degradation mechanism of this semi-crystalline polymer. It is reported that successive processing of polyethylene can cause degradation due to crosslinking or chain scission of high molecular weight fractions and this depends on whether the polymer is synthesised using a Cr catalyst (Phillips process) or Ti-catalyst (Ziegler process), (Moss and Zweifel, 1989). More evidence to support the degradation mechanism of recycled polyethylene produced by the Phillips process and the Ziegler Natta process, was published by Pinheiro *et al*, 2004. It was reported that the origin of all chain scission mechanism in polymers is due to the oxygen attack on the polymeric chain creates alkoxy and peroxy free radicals. These free radicals can abstract a hydrogen atom from the polymer chain and form chain scission. The formation of chain branching or crosslinking is a different mechanism and this happens when the alkyl free radicals add to the vinyl groups with in the polymer chain. Hence Pall Europe avoid the use of recycled polymer feedstock for making filter components to avoid processing related quality issues.

3.5. QUALITY ASSESSMENT OF PLASTIC PROCESSING

All Pall Europe filter comprise polymeric components which are injection moulded before assembly. Hence filter quality is dependent on the quality of the processing. In the early nineteen nineties quality assessment of plastic processing has been the main subject of many research papers. Compounding is an important step in plastic processing and this is mainly carried out by intermixing, extrusion or injection moulding. In the extrusion process mixing is often considered to be inefficient due to the non-uniform shear stains in the screw barrel assembly. The efficiency of mixing can be improved by incorporating mixing sections into the screw so that better dispersion and distributive mixing can be achieved. In the case of the injection moulding process the quality of mixing can be enhanced by optimisation of processing parameters such as back pressure, screw rpm and melt temperature. According to Latif & Saidpour (1996), it is essential that the quality of mixing during injection moulding process needs to be assessed as poor mixing may lead to the following issues

I. Regions of insufficient mixing can act as points of weakness and cause product failure
II. Extra processing time which may require more energy and could cause loss in the production capacity
III. More compounding additives are required in order to ensure minimum quality is maintained.

The quality of filler dispersion on a twin screw has been assessed by Essa and Hornsby (1987) where they studied the effect of processing conditions such as temperature, screw speed and various screw designs on the degree of dispersion. It has been suggested that better dispersion can be achieved by increasing the screw speed, hence better mixing can be achieved during extrusion process with increased pressure flow.

There are different ISO, BS and ASTM standards for measuring the quality of plastic

mixing. Visual inspection of colour or texture and mechanical testing such as impact, tensile and compressive are some of the commonly used test methods but these methods can only give a snap shot of quality of the product. Analytical techniques such as optical microscope, SEM, DSC are currently used to study the dispersion and distribution of additives to asses the quality of the mixing.

3.6. QUALITY CONTROL OF PLASTIC PROCESSING

Pall Ilfracombe has done significant amount of work to establish quality control methods within the factory and external suppliers for better quality polymer processing. Ohshima and Tanigaki (2000) have studied the quality control in a polymer production process. A medium scale production process consists of several reactors, blenders, dryers and extruders. By passing through each production process the quality of the polymer can be affected. Therefore polymer quality should be controlled consistently throughout the process to avoid batch to batch variation in the final product.

There is a strong need for quality modelling in a polymer processing unit. Minor changes in processing conditions could affect the rheological properties of the polymer. According to Ohshima and Tanigaki (2000) “rheology plays an important role in bridging a gap between molecular properties and rheological properties, which are close to end user quality”. Table 3.1 shows a qualitative relationship between molecular properties and polymer properties of polyethylene, published by Soga *et al*, (1993).

	Molecular structure	Molecular weight (M_w)	Molecular weight distribution	Branching chemicals	Degree of branching	Degree of branching distribution	Long-chain branching (LCB)
Mechanical and chemical property	Transparency	o	o	o	o	o	
	Tensile strength	o	o	o	o	o	o
	Impact strength	o	o	o	o	o	o
	Rigidity				o	o	
	Heat resistance				o	o	
	Cold resistance	o	o	o	o	o	
	Chemical resistance	o	o	o	o	o	o
	Heat seal	o	o	o	o	o	
Processability	Bubble stability	o	o				o
	Draw-down	o	o				o
	Extrusion torque	o	o				o

Table 3.1 Relationship between molecular structure and product properties of polyethylene- {Soga et al, 1993}

As illustrated in the above table the final properties of the polymer strongly depend on the molecular structure as well as molecular weight/ molecular weight distribution. Therefore the operating conditions of each processing unit need to be carefully optimised to achieve desirable end user properties. Pall Europe use external injection moulders so optimum processing conditions are essential to avoid molecular changes in the chemical structure of the polymer.

3.7. CONTAMINATION ISSUE

A variety of polymer additives are added in the polymer formulation for performance improvements. This includes antioxidants, pigments, processing oils and heat stabilizers which can leave a residue in the processing equipment and potentially contaminate the moulded parts which are processed in this equipment. Using contaminated moulded parts will affect the quality of the end product (filter modules). There are quality procedures developed to avoid the occurrence of these type of contamination in moulded parts. One method is periodic cleaning of processing equipment to prevent the accumulation of residues in the processing equipment. Another approach is to purge the processing equipment in a fixed time interval. Various cleaning methods were patented by Bailey and Okla, (1989) and described in the patent “Process for cleaning processing equipment”. Pall Europe has implemented various cleaning procedures within external suppliers to avoid contamination issues during processing.

3.8. CHAPTER SUMMARY

This chapter has covered the theory of thermo-oxidative and thermo-mechanical degradation of several polymers used in the manufacture of polymeric filter modules. Degradation mechanisms of virgin and recycled polymers are different and the applications where recycled polymers cannot be used for making products were discussed in this chapter. Contamination of polymers with a variety of polymer additives such as pigments and antioxidants can cause the rejection of a whole batch of filter components. This chapter discussed the importance of implementing various cleaning procedures within external filter component suppliers to avoid contamination issues during processing. The following methods were discussed in this chapter to tackle the process related quality issues at Pall Ilfracombe.

a) Importance of setting up an in-house materials characterisation facility for quality assessment.
b) Use of analytical techniques to assess the quality of the raw materials and filter components.
c) Establishment of quality control methods within the factory and external suppliers for better quality control in polymer production process.

CHAPTER 4. METHODS OF POLYMER CHARACTERISATION

4.1. INTRODUCTION

As part of the KTP program, a new materials characterisation laboratory facility was established within Pall Ilfracombe for the quality assurance of raw materials and moulded parts for the manufacture of filtration systems. A Capital Expenditure (CAPEX) was raised and approved for ordering Fourier Transform Infra Red (FTIR), Hot Stage Microscope (HSM), Dynamic Mechanical Thermal Analyser (DMTA) and identiPol-QA equipment for materials characteristion and bench marking. The function of these analytical tools is described in detail below. Within 12 months of the start of the KTP project, all the equipment was installed and a bench mark was established for all the different grades of Polyesters, Polypropylenes and Nylons used for manufacturing the filter systems. After the establishment of the materials characterisation facility, various quality- related problems were assessed and the root cause was investigated.

For detailed assessment of all the materials issues in relation to the production process, it was agreed to set up an advanced materials characterisation facility. Another CAPEX was approved and the money was spent on purchasing Gel Permeation Chromatography (GPC), Thermo Gravimetric Analysis/ Differential Scanning Calorimetry (TGA/DSC) and three more identiPol-QA units for the QC of thermoplastics within the three Pall suppliers who injection mould filter components.

This chapter introduces various polymer characterisation methods and the establishment of a materials characterisation facility at Pall Ilfracombe to investigate materials and process related quality issues.

4.2. CHEMICAL CHARACTERISATION – INFRARED SPECTROSCOPY (FT-IR)

FT-IR stands for Fourier Transform Infrared Spectroscopy. IR radiation is passed through a sample and some of the infrared radiation is absorbed by the sample and some of it passes through. The resulting spectrum represents the molecular absorption and transmission of infra-red radiation and this creates a molecular fingerprint of the sample. Like a fingerprint no two unique molecular structures produce the same infrared spectrum.

FT-IR spectroscopy is an extremely versatile and valuable tool for the characterization of polymeric structure (Fawcett, 1996). Using FT-IR it is possible to identify unknown materials, determine the quality or consistency of a sample and determine the amount of components in a mixture. Advantages of FT-IR spectroscopy is well documented in the literature (Fawcett, 1996, Siesler, 1980). Some of the major advantages of FT-IR spectroscopy include:

Speed: Most measurements by FT-IR are made in a matter of seconds rather than minutes because all of the frequencies are measured simultaneously.
Sensitivity: The sensitivity of FT-IR is very high. The detectors employed are highly sensitive and the optical throughput is very high which results in much lower noise levels and fast scanning rates.
Mechanical simplicity: The moving mirror in the interferometer is the only continuously moving part in the instrument. Thus, there is very little possibility of mechanical breakdown.
Internal calibration: These instruments are self-calibrating and never need to be calibrated by the user.

The above mentioned advantages make measurements made by FT-IR extremely accurate and reproducible. Thus FT-IR is a very reliable technique for positive identification of virtually any sample. Due to high sensitivity of IR, even the

smallest of contaminants can be identified. This makes FT-IR an invaluable tool for quality control or quality assurance applications and is very useful tool for use within Pall Ilfracombe to make batch-to-batch comparisons to quality standards or for analysing unknown contaminants.

The PerkinElmer Spectrum 100 Series FT-IR spectrometer was installed within the materials characterisation lab for the chemical characterisation of polymers. FTIR spectra for polypropylene, polyesters and nylons were generated and benchmarks for these polymers were established. These bench marks are used to check the quality of incoming raw materials and finished parts. Typical FTIR spectra for polypropylene, polyester and nylon are described below.

POLYPROPYLENE

Polypropylene is a well know commodity plastic which is manufactured by the polymerisation of propylene using a Ziegler-Natta catalyst. Polypropylene is available in three different forms a) isotactic b) syndiotactic and c) atactic. The melting point of isotactic polypropylene is 208°C and it is highly crystalline. The products manufactured using polypropylene can be sterilised making this material suitable for manufacturing filters for pharmaceutical applications. Polypropylene is resistant to many chemicals such as acids, alkalis and oils but less resistant to oxidation. The thermal degradation of polypropylene and the use of FTIR spectroscopy to study the degradation behaviour have been detailed by He *et al*., (2005), Hatanaka et al., (1999), Abdel-Hamid (2005) and Khoyluu and Katbab (1993). Figure 4.1 shows a typical FTIR spectrum of polypropylene.

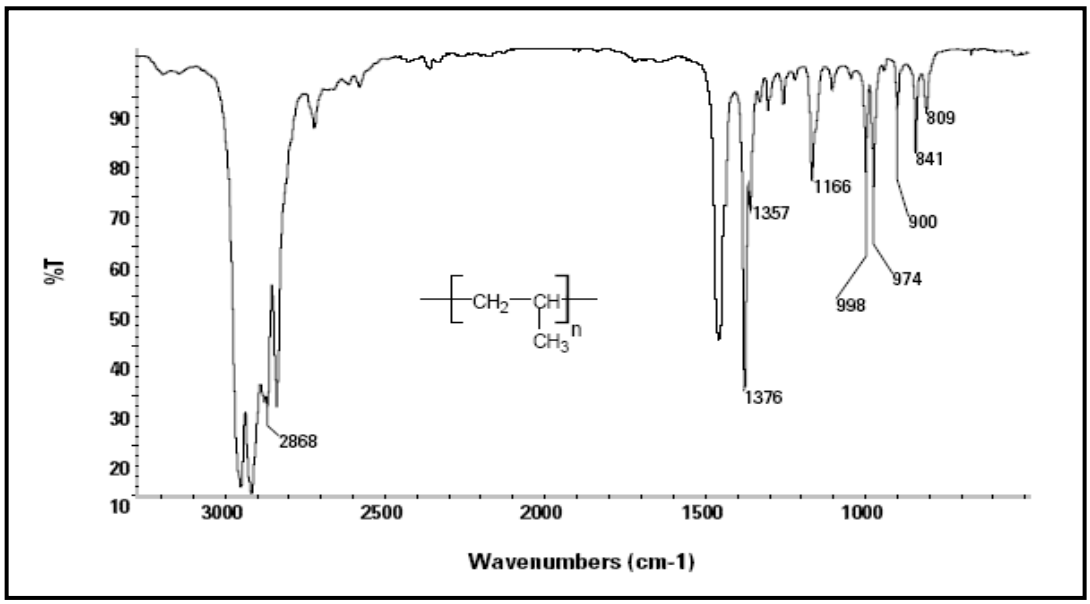


Figure 4.1 – FTIR spectrum of polypropylene (Del Fanti, 2010).

The structure of polyethylene is a chain of methylene units terminated at each end by methyl groups. Since the polymer is composed almost completely of methylene groups, its infrared spectrum would be expected to consist solely of methylene stretches and bends. The addition of a methyl side group on every other carbon atom in polyethylene gives polypropylene and this complicates the infrared spectrum . In polypropylene, in addition to the methylene group, there are methyl and methyne groups present. The bands of CH_2 and CH_3 are very intense, but there is overlap between them. The methyl peaks (CH_3 group) appear at 2956, 2880 and 1450 [cm^{-1}] and CH_2 group appear at 2925, 2868 and 1434 [cm^{-1}] *(Del Fanti, 2010)*

POLYESTER

Polyesters (polyethylene terepthalate, PET) are synthesised by poly-condensation reaction between a dicarboxylic acid and a diol. Polyesters are of two types a) aliphatic polyester and b) aromatic polyesters. The melting point of aliphatic polyester is in the range of 50–80^{o}C whereas the melting point of aromatic polyester is in the range of 265^{o}C. This significant increase in melting point synthesised by incorporating aromatic groups is due to the stiffening of the polymer back bone. Even though polyester is very resistant to heat and moisture and virtually resistant to

many chemicals, hydrolytic degradation and the effect of humidity on thermal degradation of polyesters are frequently investigated using FTIR and specified in the literature (Partini and Pantani, 2007, Arii. and Masuda, 2004). The thermal decomposition of polyester has received plenty of attention and a large number of studies have been carried out to understand the decomposition mechanism (Botelho *et al*., 2001, Holland, and Hay, 2002, Suyama *et al*., 2007). Figure 4.2 shows the FTIR spectrum of polyethylene terepthalate (PET).

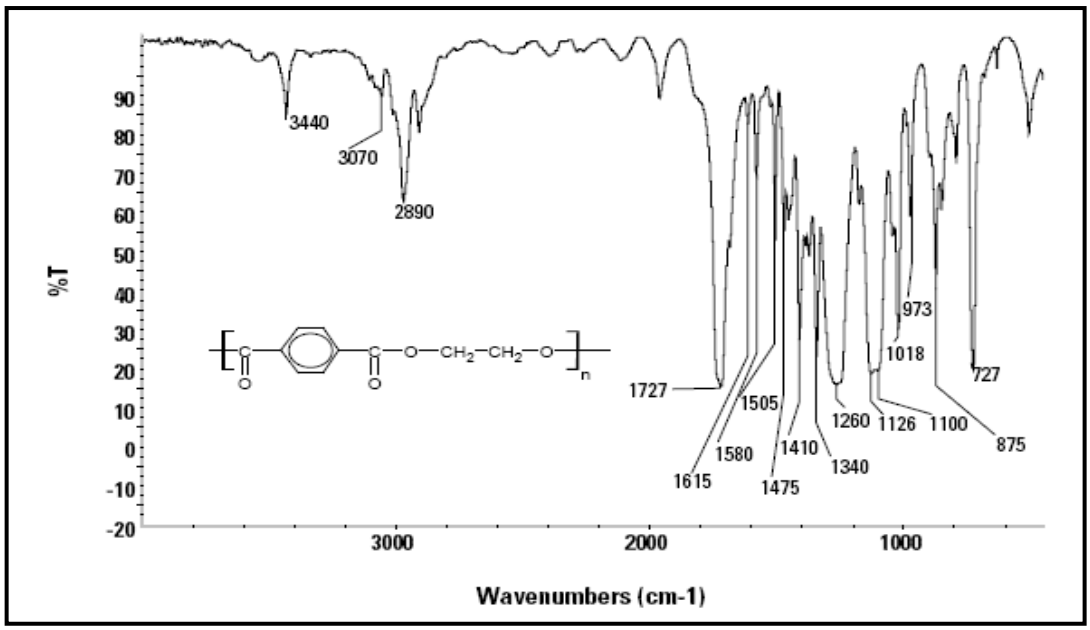


Figure 4.2- FTIR spectrum of Polyester (PET) (Del Fanti, 2010)

Both PET and polybutylene terephthalate (PBT) are generally called polyesters. The C=O bond is visible at 3440 and 1727 [cm^{-1}] and the CH aromatic group is visible at 3070[cm^{-1}]. Transmission peaks at 2890, 1470, 1340 [cm^{-1}] indicate the presence of CH_2 group within polyester. The second strongest peak at ~1,260 [cm^{-1}] is generally described as the asymmetric C-O-C stretch *(Del Fanti. N.A, 2010).*

POLYAMIDES (NYLON)

Polyamides are synthesised by the polycondensation reaction between dicarboxylic acid and diamines. Nylons are known as aliphatic polyamides and normally nylons are represented by a numbering system. The number indicates the number of carbon atoms present in the monomer units. Nylons used at Pall Ilfracombe are Nylon 6 10 and Nylon 6 11, the first number indicates the number of carbon atoms in the amine group and the second number indicates the number of carbon atoms in the acid group. Nylon has very good tensile strength, abrasion resistance and resistant to many solvents. Nylon is well known for its moisture absorption property. The plastic deformation behaviour of nylon due to the effects of moisture absorption has been studied and many papers have been published in this area (e.g. Miri *et al*., 2009, Jia and Kagan**,** 2001). The durability of nylon parts subjected to radiation needs to be understood before considering it for sterilisation under gamma irradiation. The effects of high energy radiation on nylons have been reported (e.g. Zaharescu, *et al*., 2010, Lihua, 1990). FTIR spectroscopy has been recognised as a valuable tool for studying the degradation behaviour of polyamides. This method has been used to study the degradation temperature of nylon end caps at Pall Corporation during the end capping and welding process thereby optimising the processing parameters. Figure 4.3 shows the FTIR spectrum of nylon 6-6 polymer.

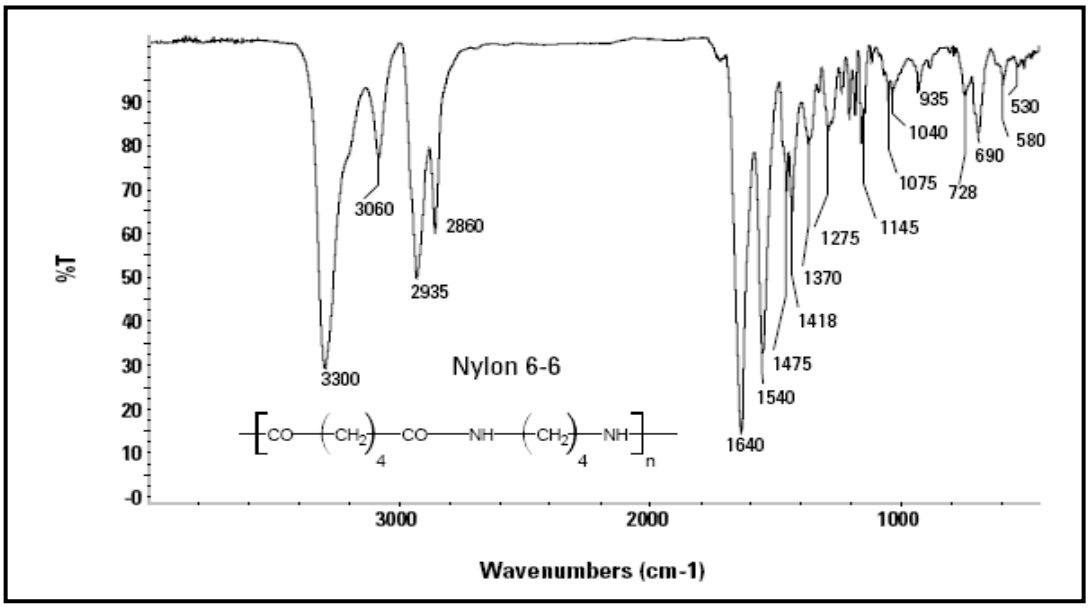


Figure 4.3- FTIR spectrum of Nylon 6-6 (Del Fanti, 2010)

The N-H group is visible at peak intensities corresponding to 3300, 1560-1540 [cm^{-1}] and C-N group corresponding to 3080- 3050 [cm^{-1}] are common to all nylons. Different nylons can be distinguished by the slight differences in frequencies between 1400[cm^{-1}] and 900[cm^{-1}] where many crystalline bands lie (Del Fanti, 2010). Therefore FTIR spectroscopy is a useful tool for monitoring batch to batch variations in feedstock.

4.3. THERMO-MECHANICAL CHARACTERISATION

4.3.1. DYNAMIC MECHANICAL THERMAL ANALYSER (DMTA)

Dynamic Mechanical Thermal Analysis (DMTA) is probably the most versatile thermal analysis method available, and no other single test method provides more information about the thermo-mechanical properties of a sample in a single test. DMTA measures the stress and strain in a sinusoidally deformed sample at different loading frequencies and temperatures. It provides information about relaxation processes in polymers, specifically at the glass transition and at sub-glass transition temperatures. This method can be used to study thermo mechanical characteristics of the polymers such a storage modulus (E'), loss modulus (E''), loss factor (tan delta) and glass transition temperature (Tg).

DMA 8000 is a Dynamic Mechanical Thermal Analyzer manufactured by Perkin Elmer and this equipment has been installed in the materials characterisation lab for polymer characterisation at Pall Ilfracombe. DMTA works by applying a cyclic deformation, usually at about 1 Hz, to a sample of known geometry. Here the sample is subjected to a controlled stress or a controlled strain. DMTA measures stiffness and damping and these properties are expressed as dynamic modulus and tan delta *(DMTA 8000, 2008)*. Figure 4.4 is a typical DMTA plot with storage modulus and tan delta plotted as a function of temperature.

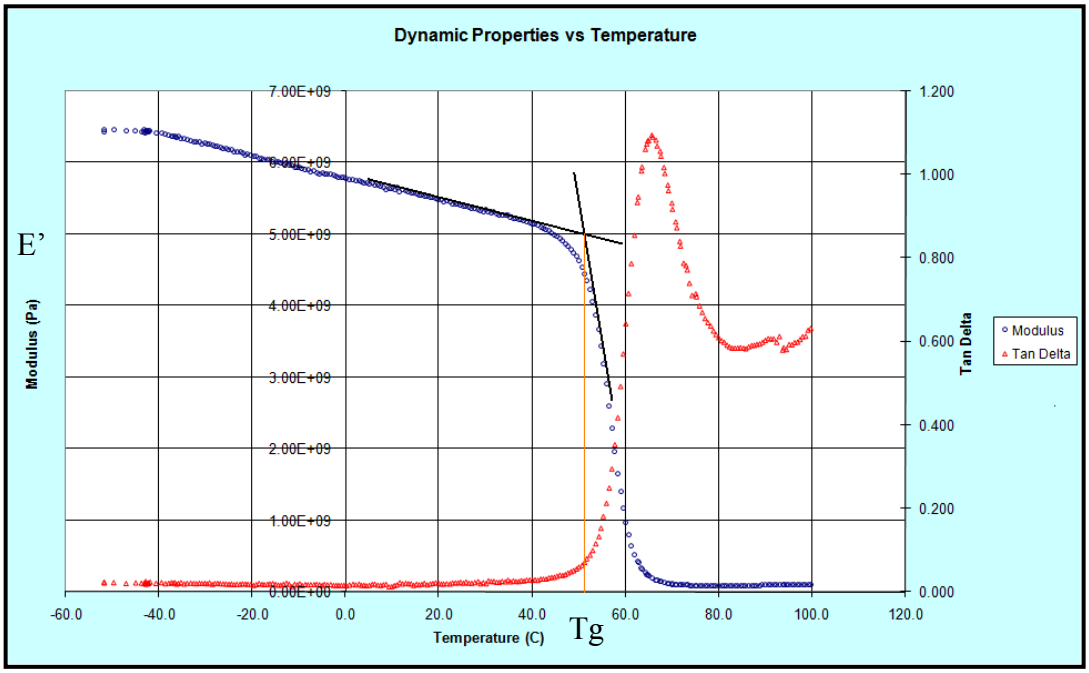


Figure- 4.4 DMTA plot of thixotropic epoxy adhesive (University of Bath) with measured Tg of 52ºC (tangent construction from the storage modulus characteristic).

DMTA is a very powerful technique to study the dynamic mechanical characteristics of polymers. This includes modulus, complex modulus, complex viscosity, damping factor and glass transition temperature. These terms are clearly explained in the literature and Luckenbach's definitions (Rheometrics, Kalsersberger.E and Netzsch-Geratebau, 1985) follow:

a) Modulus- The modulus is defined as the ratio of stress to strain. The ratio of the elastic stress to strain is the elastic modulus E' and the ratio of the viscous stress to strain is the viscous (or loss) Modulus E"

b) Complex Modulus. The complex modulus E* = E' + iE" reflects the contribution of both elastic and viscous components to the material's stiffness.

c) Complex Viscosity. The complex viscosity is a measure of the material's overall resistance to flow as a function of shear rate.

d) Damping Factor. The ratio of the viscous modulus to the elastic modulus is the tangent of the phase angle shift between the stress and strain vectors. Thus, E"/E'= tan delta. This measures the damping capability of the material.

e) The Glass Transition temperature. The effect of the polymer's glass transition can be clearly observed during the measurement of the storage modulus E'. The glass transition is a reversible change of the polymer between the rubbery and glassy states and the temperature at which this occurs is called the glass transition temperature Tg. DMTA is considered the most sensitive method for measuring a material's glass transition temperature. The glass transition is detected as a sudden change in the elastic modulus of the polymeric material, i.e. softening. Therefore the glass transition temperature is a key factor in deciding the processing parameters of a polymer.

Principles of DMTA

The response of a liner viscoelastic material when subjected to a cyclic loading is shown in the figure 4.5 below

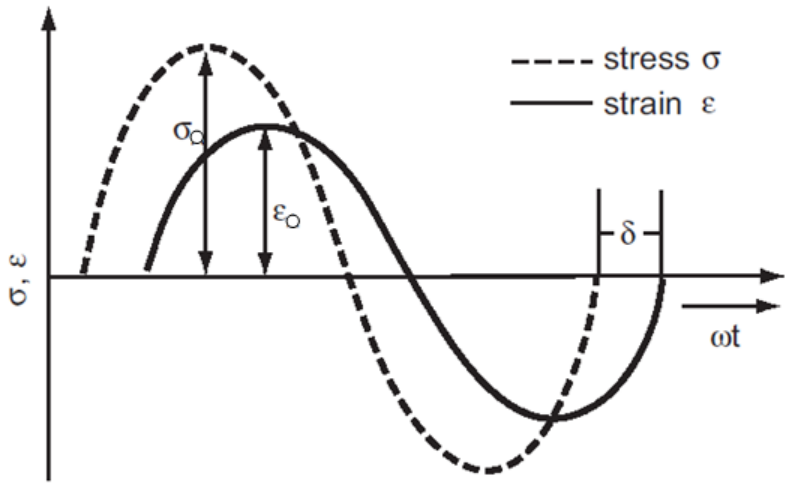


Figure 4.5 Response of a linear viscoelastic material (Principles of DMA, 2004)

$\varepsilon = \varepsilon_o \sin \omega t$ ……..(1)

$\sigma = \sigma_o (\sin \omega t + \delta)$ …….(2)

δ = Phase angle

ω = Frequency

$(\sigma_o / \varepsilon_o) = |E|$ (Absolute value of the dynamic modulus) …… (3)

For a perfectly elastic material phase angle (δ) = 0. Figure 4.6 shows the stress strain behaviour of a purely elastic material.

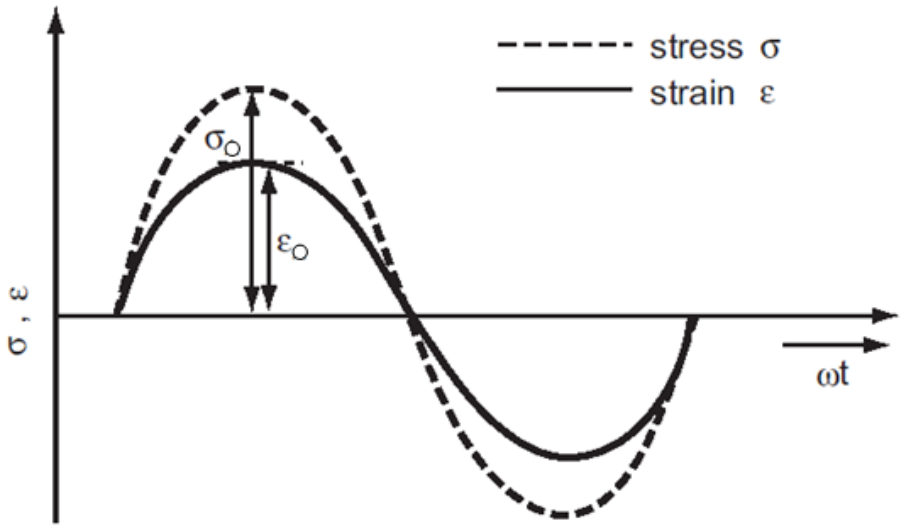


Figure 4.6: Stress strain response of a purely elastic material {Principles of DMA, 2004}

From equation (2) and (3) $\sigma = \varepsilon_o |E| (\sin \omega t + \delta)$

$= \varepsilon_o |E| [\sin \omega t \cos \delta + \sin \delta \cos \omega t]$

$= \varepsilon_o \sin \omega t (|E| \cos \delta) + \varepsilon_o \cos \omega t (|E| \sin \delta)$

$E' = |E| \cos \delta$ (storage modulus) .....(4)

$E'' = |E| \sin \delta$ (loss modulus) .....(5)

From (4) and (5) $\tan \delta = E'' / E'$ (Stark and Jaunich, 2011)

E’ relates to component of strain in phase with stress associated with elastic energy stored in material

E” relates to component of strain 90° out of phase with stress associated with energy dissipated per cycle

tan δ represents the mechanical damping in a viscoelastic system.

Using DMTA the stress relaxation and creep of the material can also be studied. Stress relaxation and creep are the most fundamental properties of viscoelastic material. The reduction in stress required to maintain a constant strain over a particular amount of time can be measured and this is called stress relaxation. Creep is exactly the opposite of stress relaxation tests. It is defined as the change is strain at a constant stress over a period of time.

Dynamic mechanical thermal analysis method is well suited to determine viscoelastic properties of solids at Pall Ilfracombe. Polymers in the form of pellets can also be tested using the DMA 8000 unit material pockets which are a unique sample preparation tool specifically designed to work with the DMA 8000. These innovative pockets allow powdered or non-self supporting materials such as powdered polymer, pellet polymer, drugs, gels and low viscosity materials, to be investigated by DMTA *(DMA 8000, 2008)*. Applications include detecting small amounts of amorphous material in samples that cannot be formed into a bar or a material naturally occurring in a powder-like state. They can also be used by creating a film or coating or filter media on the inside surface to allow the film to be studied easily. This enables media to be characterised at Pall Ilfracombe and provides insight into the root cause for media-related quality issues.

4.4. THERMAL CHARACTERISATION

Thermal analysis techniques have been used for many years for characterization of

polymer materials. DSC and TGA are thermal analysis methods routinely used to characterise the thermal stability of polymers to allow prediction of material lifetime.

4.4.1 DIFFERENTIAL SCANNING CALORIMETRY (DSC)

DSC is a commonly used characterisation method to investigate the heat related properties of polymers. DSC measures the energy necessary to establish zero difference in temperature between a substance and an inert reference material. Here the two specimens are subjected to identical temperature environments which is heated or cooled at a controlled rate. DSC is a highly sensitive test which requires very small amount (2 to 20mg) of sample for the test. According to Chen *et al*, (1996) higher sensitivity does not always means that better result will be obtained in a DSC. They have studied the importance of baseline calibration in a DSC for more accurate results.

There are two types of DSC systems in common use and Figure 4.7 shows the pictorial representation of these two systems:

a) Power compensation DSC and
b) Heat flux DSC.

In power compensation DSC the temperatures of the sample and reference are controlled independently using separate, identical furnaces. The temperatures of the sample and reference are made identical by varying the power input to the two furnaces but in the case of heat flux DSC, the sample and reference are connected by a low resistance heat flow path (Bhadeshia, undated). In both cases DSC measures the change of temperature difference between the sample and the reference during isothermal or non isothermal conditions. This temperature difference can be used to detect the melting (Tm), glass transition (Tg) and crystallisation (Tc) properties of a polymer (Stark and Jaunich, 2011).

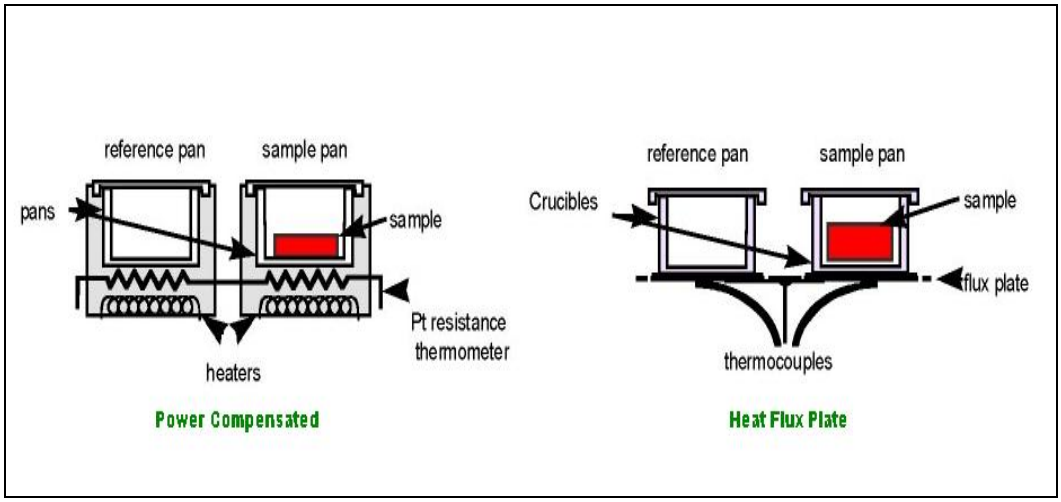


Figure 4.7: Types of DSC taken from Materials Solutions, NPL {National Physical Laboratory (NPL), 2004}

Glass transitions occur as the temperature of an amorphous polymer is increased. These transitions appear as a step in the baseline of the DSC signal and this is due to the sample undergoing a change in heat capacity. Figure 4.8 is a schematic DSC curve demonstrating the appearance of Tg, Tc and Tm.

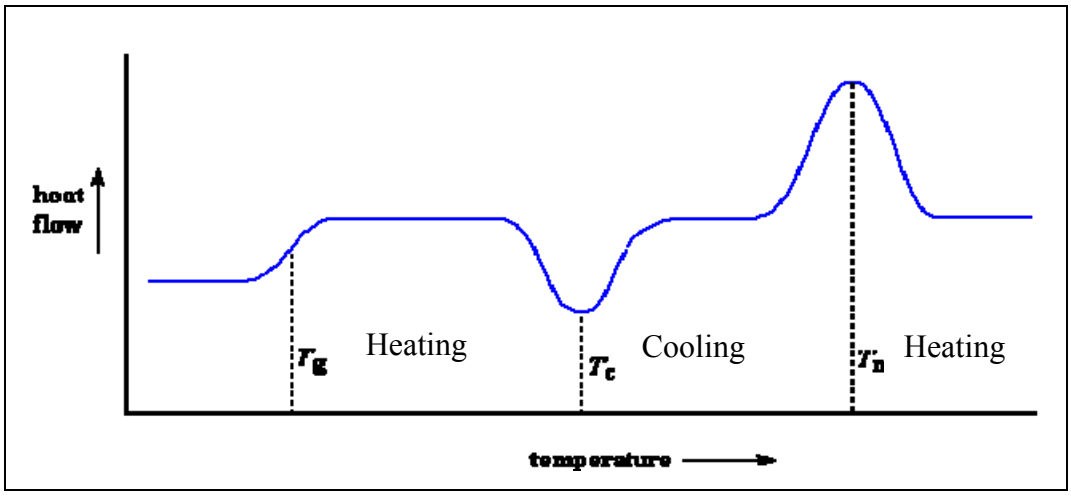


Figure 4.8: Schematic DSC curve demonstrating the appearance Tg, Tc and Tm (National Physical Laboratory (NPL), 2004}

As the temperature increases amorphous polymers will become less viscous and at some point the molecules may obtain enough freedom of motion to spontaneously arrange themselves into a crystalline form. This is known as the crystallization temperature (T_c). This transition from amorphous solid to crystalline solid is an exothermic process and this result in a peak in the DSC characteristic (Figure 4.8). As the temperature increases the sample eventually reaches its melting temperature (T_m). Aref-Azar *et al* (1996) has explained the use of DSC to measure the physical aging in amorphous and crystalline polymers. It is reported in this literature that during physical aging the degree of crystallinity and melting point of the polymer changes and this can be related to the enthalpic relaxation in the amorphous and crystalline regions. The melting process results in an endothermic peak in the DSC curve. Pall Ilfracombe uses DSC to measure the Tm and the oxidation behavior of various thermoplastics to find the optimum processing temperature for end-capping and welding of filter modules.

4.4.2 SIMULTANEOUS THERMAL ANALYSER (STA 6000)

Differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), differential thermal analysis (DTA), thermo-mechanical analysis (TMA) and dynamic thermal analysis (DMA) are widely employed in both scientific and industrial sectors *(Dobkowski, 2006)*. STA 6000 is a new equipment developed by Perkin Elmer which can acquire both DSC and TGA results simultaneously. The working principle of DSC and TGA are explained in section 3.3.1. The applications of DSC and TGA for thermal stability characterisation of polymers are explained in the literature (e.g. Wong and Lam, 2002, Fleszar, 2000, Golebiewski and Galeski, 2007).

The STA 6000 from Perkin Elmer has been installed within the materials characterisation lab at Pall Ilfracombe to study the following characteristics of polymers used for making the filter modules.

I. Compositional analysis: quantitative content analysis
II. Decomposition temperatures: the temperature at which material starts to degrade
III. Filler content: especially when blending the plastic with masterbatch
IV. Lifetime predictions: using TGA kinetics software
V. Thermal/Oxidative stability
VI. Glass transition, crystallisation and melting behaviour

Figure 4.9 is a DSC/TGA plot generated using STA6000 equipment as part of a study on the degradation behaviour of PP1052 grade polypropylene before and after processing.["Sample a" is unprocessed PP1052 pellets, "Sample b" is injection moulded filter cage material manufactured using PP1052 and "Sample c" is slightly degraded injection moulded filter cage material manufactured using PP1052]

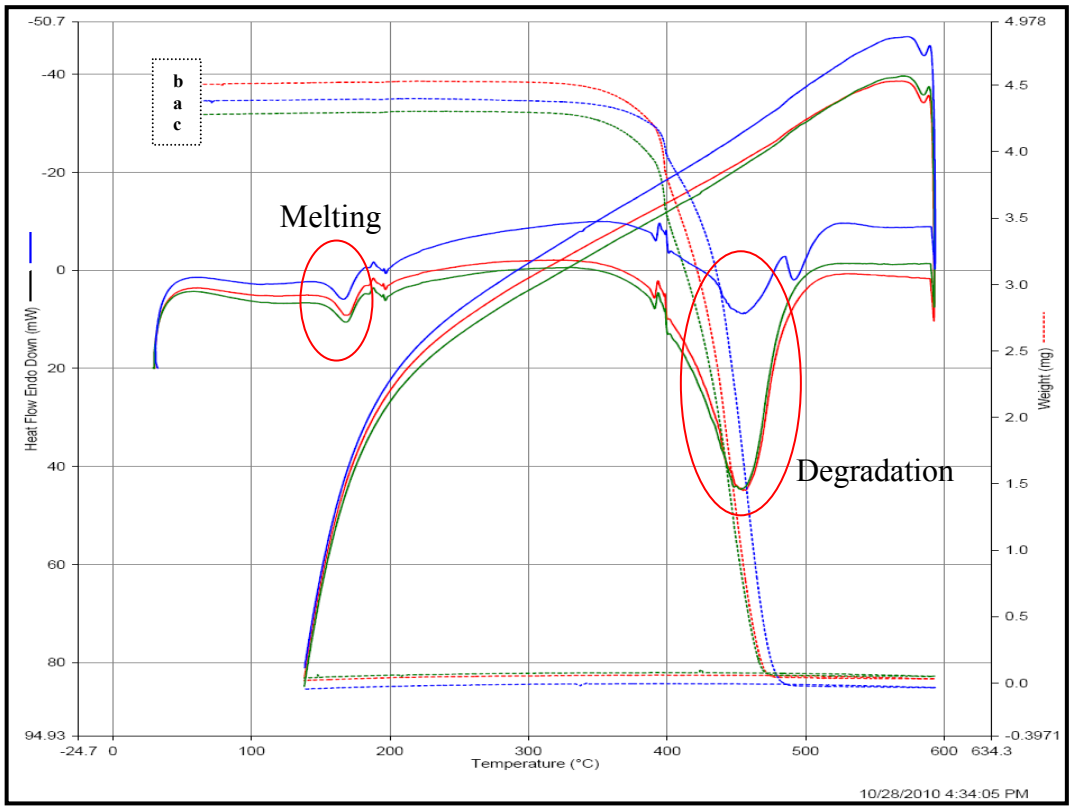


Figure 4.9 Typical DSC-TGA plot for a degradation study on polypropylene.

As explained in this chapter, section 4.4.1 DSC is a thermoanalytical technique which can be used to study the phase transitions within the polymer. Using DSC it is possible to observe the Tg, Tc, Tm and oxidative degradation of the polymer when temperature is increased at a constant rate. From the above DSC/TGA graph as the temperature increased the sample has reached the melting temperature and this resulted in an endothermic peak at ~ 165°C. As the temperature increased further, the sample eventually reached at its degradation point and resulted in another endothermic peak at ~450°C in the DSC curve. DSC can also be used to study the oxidative stability of the polymer. In this test polymer sample is brought to a desired temperature under an inert atmosphere and then oxygen is added to the system. The oxidation process can be clearly observed by measuring the deviation in the baseline. TGA measures the change in mass of the sample as a function of temperature or time in a controlled atmosphere. This technique is mainly used to study the thermal stability of each component within the polymer. The above TGA graph shows the mass loss of three different polymeric samples at a temperature of ~ 375°C due to decomposition. It is very clear from the graph that "sample a", unprocessed PP1052 is more thermally stable than "sample c" which is a slightly degraded injection moulded PP1052 based filter cage.

4.5. OTHER CHARACTERISATION METHODS

4.5.1 MELT FLOW INDEX (MFI)

Grellmann and Seidler, (2007) explained that the flowability or flow behaviour of fluid can be characterized by the viscosity that describes the internal resistance of a fluid to an external acting load. Corresponding to the type of loading, it is possible to distinguish shear and elongational viscosity. Polymer melts normally exhibit Newtonian behaviour (Newtonian fluids are those fluids whose viscosity remains constant when shear rate varies). But in real processing such as extrusion or injection moulding, the shear rate is much higher and this changes the viscosity of the polymer and the flow become non-Newtonian. The relationship

between shear stress and shear rate for describing the flow behaviour of a polymer melt can be studied using various methods. MFI is a special version of capillary rheometer used for characterising thermoplastics.

Melt Flow Index is considered as an indirect way of assessing the average molecular mass and is an inverse measure of the melt viscosity. A high MFI indicates a low viscosity and more polymer flows under the test conditions. MFI is a critical parameter to be considered for choosing the processing method and generally higher MFI polymers are used in injection moulding and lower MFI polymers are used with blow moulding or extrusion processes. Many factors affect the flow properties of polymers. Molecular weight distribution, the presence of co-monomers, the degree of chain branching and crystallinity influence a polymer's MFI (Shenoy and Saini 1986).

The MFI-10/230 melt flow indexer from Lloyd instruments Ltd has been installed and used to determine the melt flow rate of polymers by extruding them in a molten state through a calibrated circular die using a reference weight. This equipment can be operated by two methods. The manual method requires the extruded polymer to be cut off at regular intervals by hand and then weighed on a standard laboratory balance. The MFI is calculated as the weight of polymer extruded in a 10 minute period, i.e. grams/10 mins. MFI 10/230 is fitted with an auto cut-off unit, auto flow rate timer (AFRT). The auto cut-off unit will automatically cut the polymer at the required time interval. The AFRT allows the unit to conform to ASTM D1238 Method B where the polymer does not have to be cut and weighed so a laboratory balance is not required.

According to ASTM D1238 Method B, Melt Flow Index is the output rate (flow) in grams that occurs in 10 minutes through a standard die when a fixed pressure is applied to the melt via a piston and a load of total mass 2.16 kg. Selection of temperature depends on the type of polymer, for example 230°C for polypropylene and some polymers are measured at a higher temperature, some use different weights and some even different orifice sizes. Pall Ilfracombe use MFI equipment in the QC lab for standard quality assurance.

4.5.2. HOT STAGE MICROSCOPY

A FP82HT Hot Stage microscope from Mettler Toledo has been installed for the thermo optical characterisation of polymers. The FP82HT Hot Stage is easy to use and has a precise thermal measuring cell for visual sample inspection. This equipment is connected to a microscope and using the video camera connected to the measuring cell, video images can be captured.

Using the hot stage microscope (HSM) the test sample can be placed between a slide and a cover glass using the method normally used in microscopy. The sample is subjected to a temperature program and observed/filmed using a video camera. Normally samples are pre-melted and made into a thin film before the test begins. HSM is a very useful equipment for studying the melting characteristics and crystallisation behaviour of polymers. When polymers crystallise from the melt, three dimensional spherical structures will form within the polymer called spherulites (Gedde, 1995). The formation of spherulites in a semi-crystalline polymer can be observed using a hot stage microscopy. Figure 4.10 shows the formation of spherulites within nylon (Zytel E55 grade from DuPont) when it is cooled from 240°C to ambient @ 5°C/min.

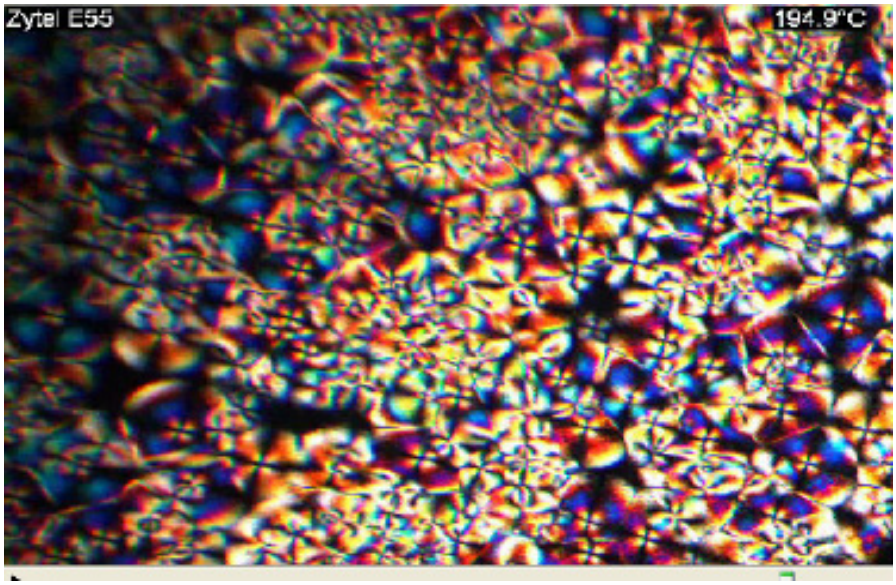


Figure 4.10- Formation of spherulites in nylon polymer

4.5.3. GEL PERMEATION CHROMATOGRAPHY (GPC)

Molecular architecture deals with the shape of the polymer molecule which is important for many properties (Gedde, 1995). Short chain branching tends to reduce the crystallinity and long chain branches have effects on rheological properties. The properties of the polymer very much depend on the size of the polymer molecules and the molecular weight of the polymer influence the melting point and mechanical properties. Rheological properties such as melt viscosity show a strong increase with increasing molar mass. This explains why high molecular weight polymers are difficult to process but they have very good mechanical properties in the final product. At Pall Ilfracombe polyethylene, polypropylene, polyester and nylons with different molecular weights are used for making different components of industrial filter assembly. The processing parameters required for end-capping/welding of high molecular weight and low molecular weight polymers are different. So it is important to understand the molecular weight or flow characteristics of the polymer to optimise various processing conditions. There are different methods employed to measure the molecular weight distribution of the polymer. Gel Permeation Chromatography (GPC) can be used to measure the whole molar mass distribution of polymers. In GPC a dilute solution of polymer is injected into a gel column. The flow through times of different molar mass species depends on their hydrodynamic volumes (Nesterov, 1987). Large molecules have little accessibility to the pores of the gel and they are eluted (come out) after a short period of time. Smaller molecules can penetrate into a much larger volume of the porous gel and they remain in the column for a longer period of time. The concentration of the polymer passing through the column is recorded continuously as a function of time by measurement of refractive index or infrared light absorption.

The molecular weight of polymers is the most important parameter for characterising the physical properties of polymers. The full representation of molecular weight distribution is only achieved using GPC. Molecular mass can be represented in four different forms a) number average molar mass b) weight average

molecular mass c) Z average molecular mass and d) viscosity average molecular mass (Gedde 1995).

The number average molecular mass is represented as
$Mn = \sum N_i M_i / \sum Ni$, Where Ni is the number of molecules of molar mass Mi

The mass or weight average molecular weight is represented as
$Mw = \sum NiMi^2 / \sum Ni\ Mi$

The Z average molecular weight can be represented as $Mz = \sum NiMi^3 / \sum NiMi^2$

While viscosity average molecular weight can be represented as
$Mv = (\sum NiMi^{1+a} / \sum Ni\ Mi)^{1/a}$

Where "a" is a constant that takes values between 0.5 and 0.8 for different combinations of polymer and solvent.

Mn and Mw of the polymers can be determined by conventional GPC method using a calibration curve of the log (molecular weight) versus elution volume of standard polystyrenes (Mori, 1980). A PL-GPC50 instrument from Agilent/Varian has been installed within the materials characterisation lab to study the molecular weight distribution of polyesters and nylons. The PL-GPC 50 Plus is a high resolution GPC system designed for operation from ambient to 50°C. This system is comprised of a precision solvent delivery system, sample injection system and high performance differential refractive index detector. PL- GPC50 is equipped with an auto sampler and control software which can be used to inject the sample automatically. Using this arrangement it is possible to define the injection parameters, graphically define the physical location of the sample and define the order of the samples to be injected. At Pall Ilfracombe GPC will be used to study the molecular architecture of many polymers to understand the physical properties of polymers as part of materials selection for new product development and quality assessment.

4.6. CHAPTER SUMMARY

This chapter has introduced various polymer characterisation methods and the establishment of a materials characterisation facility at Pall Ilfracombe to investigate materials and process related quality issues. Table 4.1 summarises the list of equipment purchased and its functions to provide, via onsite materials characterisation, a better understanding and creates a general awareness of the material's physical, chemical and thermal behavior.

Table 4.1 Materials characterisation methods and its functions

METHODS	INSTRUMENT	FUNCTION
CHEMICAL CHARACTERISATION	FT-IR	a) Identify unknown materials b) Determine quality and consistency of a sample c) Determine the amount of components in a mixture
THERMO-MECHANICAL CHARACTERISATION	DMTA	a) Dynamic mechanical characterisation of polymers b) Determination of viscoelastic properties of polymers c) Study of complex modulus and glass transition temperature of polymers
THERMAL CHARACTERISATION	DSC	a) Study melting point, crystallisation temperature and glass transition temperature of polymers b) Study oxidation behavior of various thermoplastics to find optimum processing temperature
	STA-6000	a) Compositional analysis b) Study decomposition temperature and filler content c) Life time predictions d) Study thermal and oxidative stability of the polymer
OTHER CHARACTERISATION METHODS	MFI	a) Study the rheology of polymers
	HSM	a) Melting and crystallisation characteristics of polymers b) Contamination analysis
	GPC	a) Study the molecular architecture of polymers b) Determine molecular weight distribution for characterising the physical properties of polymers

The application of these methods to characterise polymeric materials and the assessment of materials related manufacturing issues are explained in chapter 5 of this thesis. Establishment of an advanced materials characterisation facility was one of the many achievements with this KTP program.

CHAPTER 5. APPLICATION OF THE ANALYSIS EQUIPMENT AT PALL

5.1. INTRODUCTION

This chapter explains various tests and analyses carried out to solve quality problems related to materials after the introduction of the materials characterisation facility at Pall Ilfracombe. It was used to determine whether the quality problems are related to a faulty manufacturing process or a raw materials issue. In this chapter several case studies of the application of the analysis equipment are explained with relevant examples.

5.2. INVESTIGATION ON BATCH TO BATCH VARIATION IN POLYMER FEED STOCK

Batch to batch variations in incoming raw materials is a common problem within most of the polymer processing industries. With the capability of polymer characterisation facility at Pall Ilfracome several batches of materials were tested to identify the variation in the incoming raw materials and moulded parts. Below mentioned are few examples of tests conducted at Pall Ilfracombe to identify batch to batch variations in moulded parts came from external suppliers.

Example 1- Investigation on the batch to batch variation in moulded end caps made of PP achieve grade material came from the external supplier.

Problem- It was reported that there was an endcapping issue in the filter assembly unit where operators cannot achieve enough melt penetration on end cap surface for the endcapping process. Manufacturing engineers suspected that the endcapping issue was related to batch to batch variation in moulded parts.

Materials received for analysis (Batch details)

1- T-9388 (New batch end cap)

2- T-9295 (Reference sample)

The following test methods were carried out to identify batch to batch variations in end caps made of PP achieve grade material.

(i) MFI Test

Melt Flow Index (MFI) test was carried out as per ASTM D1238 standard on both samples and the results are shown in table 5.1. MFI is an indirect measure of molecular weight of the polymer. Higher the MFI indicates lower the molecular weight.

Table 5.1: Average in-house MFI test results for polypropylene

MATERIAL	T-9388	T-9295
MFI (g/10min)	21.71	21.395

Based on the MFI test results there is no significant variation in flow properties of both the current and reference samples.

(ii) DMTA Analysis

DMTA analysis was carried out to study the glass transition temperature (Tg) of the polypropylene. DMTA is considered as the most sensitive method for measuring the Tg of the polymer. Tg is measured as the sudden and noticeable change in storage modulus from the DMTA graph. From the test results below (Figure 5.1 and Figure 5.2) it is very clear that the Tg of the both samples tested are approximately -15°C, which is the same as what is specified in the data sheet for PP.

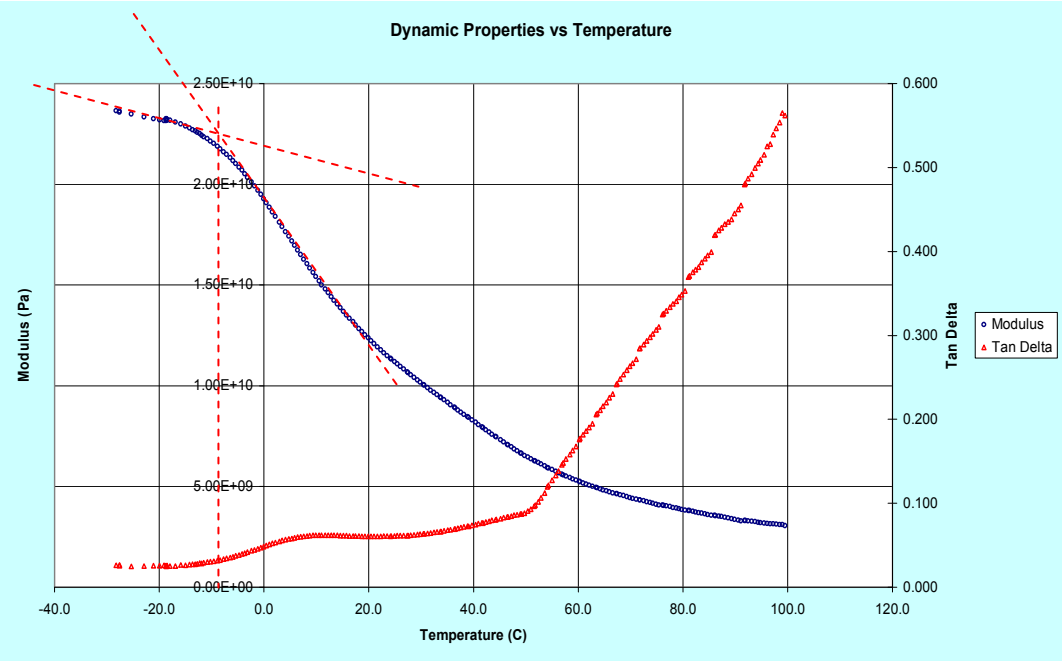


Figure 5.1- DMTA graph for PP-T-9295

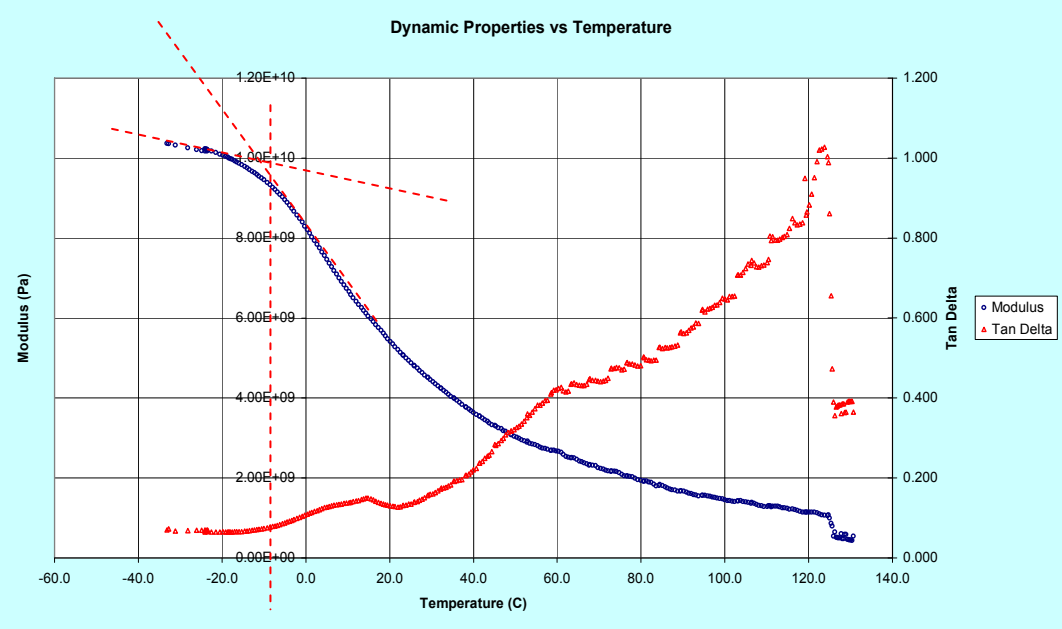
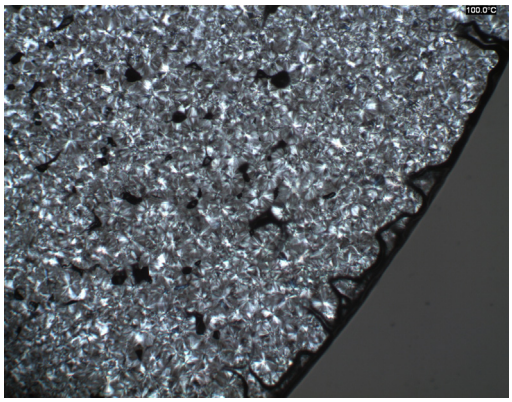


Figure 5.2 DMTA graph for PP-T-9388

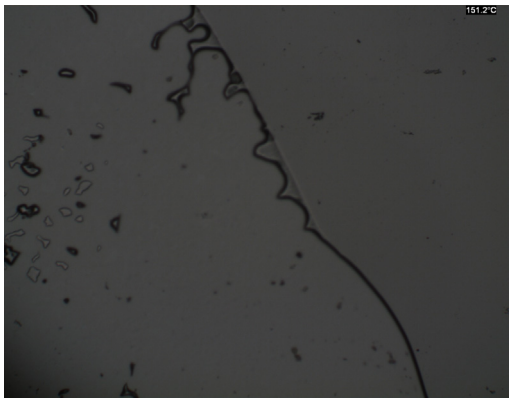
(iii) Hot stage microscopy

As described in chapter 4 (Section 4.5.2) of this thesis, hot stage microscopy is a very powerful equipment for the visual characterisation of material's thermal

transition. In this study, hot stage microscopy is used to determine the melting characteristics of polypropylene. PP samples were heated up to 180^{o}C at 5^{o}C/min and kept at 180^{o}C for 5 minute. The samples were cool down to 100^{o}C at 5^{o}C/min and kept at 100^{o}C for 5 min. At this stage spherulites were clearly visible. Figure 5.3 and figure 5.4 shows the formation of spherulites in tested polypropylene samples. This sample was again heated up at 5^{o}C/min and carefully observed the temperature at which the spherulites disappeared. It was observed that the spherulites disappeared at ~151^{o}C which indicates the melting point of polypropylene. Both batch showed similar thermal transitions which again indicates the melting characteristics of both polymers are same.

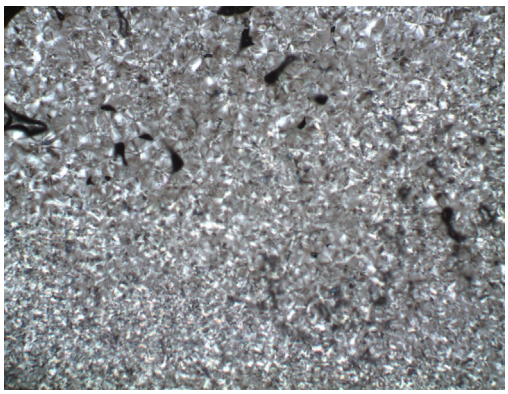


PP T-9388(100°C)

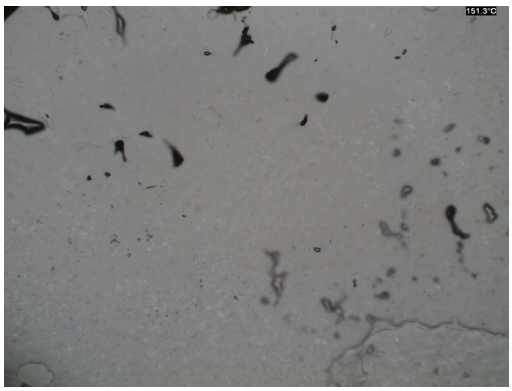


PP T-9388 (151°C)

Figure 5.3 Formation of spherulites in PP-T-9388 batch sample



PP T-9295 (100°C)



PP T-9295 (151°C)

Figure 5.4 Formation of spherulites in PP-T-9295 batch sample

(iv) FTIR Analysis

FTIR analysis was carried out to find the purity of the polypropylene sample. Two samples were tested and spectrums was analysed. Figure 5.5 shows the combined spectrum of T-9388 and T-9295 PP achieve samples. No major changes in the % transmittance peak have been noticed between the two spectrums.

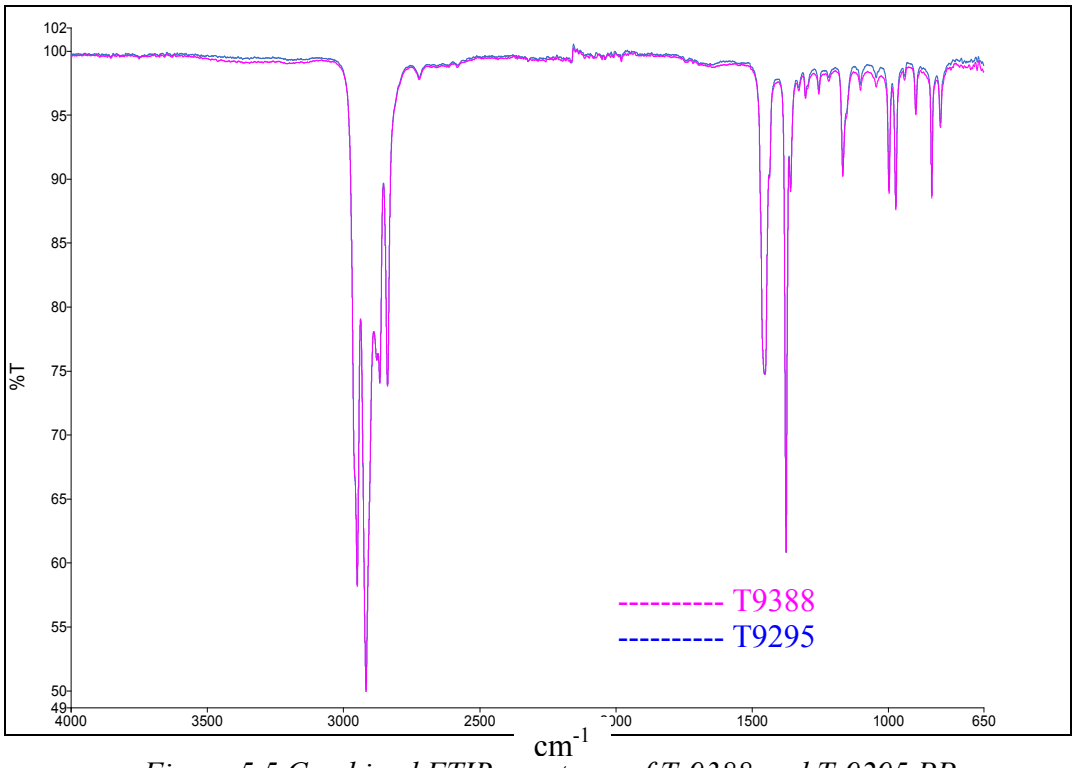


Figure 5.5 Combined FTIR spectrum of T-9388 and T-9295 PP

Conclusion

FTIR, MFI, DMTA and hot stage microscopy analysis have showed no significant difference in chemical characteristics or physical properties between T-9388 and T-9295 moulded parts. Therefore it was concluded that the end capping issue was related to the manufacturing process. The issue was later rectified by calibrating the machine set conditions.

Example 2 – Investigation on thermal aging characteristics of LDPE MT10 material using FTIR spectroscopy.

The following samples were tested using FTIR and spectra were analysed to understand the thermo-oxidative degradation in polyethylene during processing.

Sample 1- MT10 Polyethylene pellets (Virgin material)

Sample 2- PSB0287/STD (Processed before ovening)

Sample 3- IN9462 (Processed after ovening 6hrs @65^{o}C)

FTIR Analysis

Fourier-Transform Infra-Red (FTIR) spectroscopy is a valuable tool to assess the chemical/thermal degradation of polymers during processing. This is done by monitoring the formation of carbonyl oxidation products due to chemical degradation reactions. It could therefore be useful to assess whether chemical degradation has occurred to the processed material during the ovening/drying process. Figure 5.6 and 5.7 shows the individual and combined spectra of all the three samples.

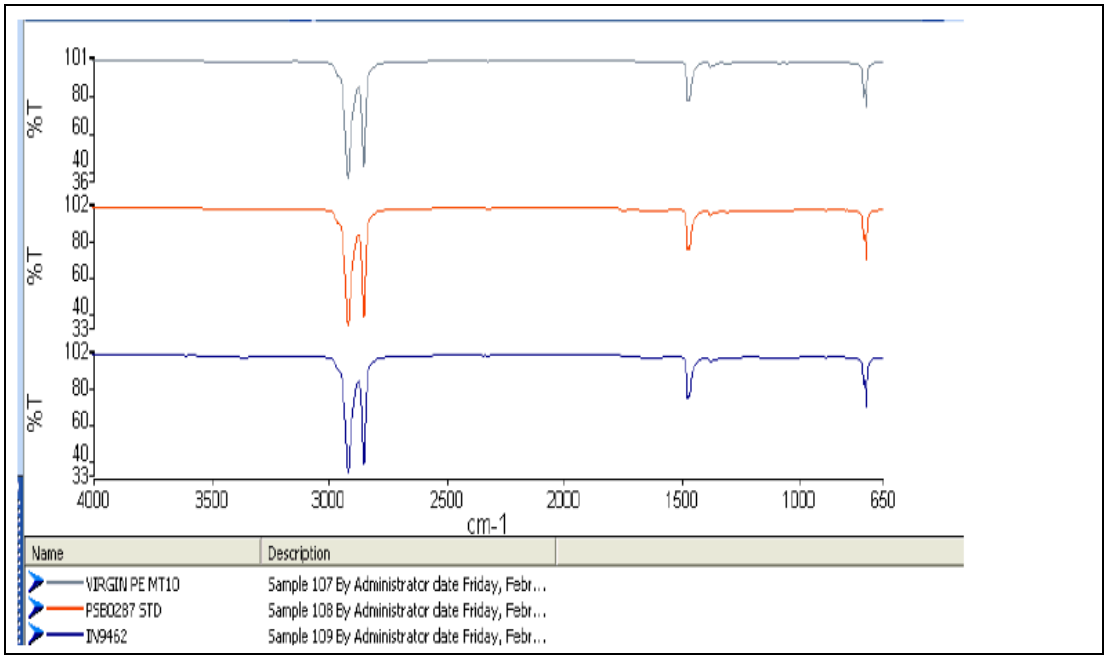


Figure 5.6 Individual FTIR spectra of all the three samples

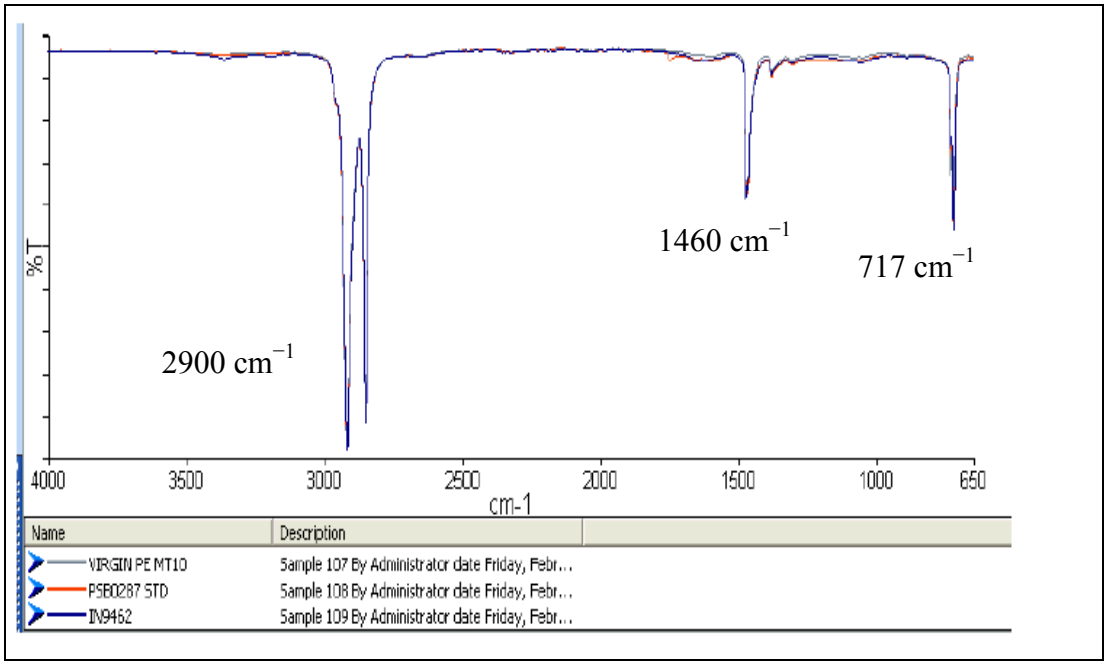


Figure 5.7 Combined FTIR spectra of all the three samples

Discussion

FTIR analysis was conducted to evaluate the degree of degradation of processed MT10 materials before and after the ovening process. Since the polymer is composed almost completely of methylene groups, its infrared spectrum would be expected to consist solely of methylene stretches and bends. The C–H stretching (2900 cm^{-1}), CH_2 deformation bending (1460 cm^{-1}) and CH rocking bending (717 cm^{-1}), which are the main peaks of polyethylene are observed for all samples (Wilkie, 1998). The result shows all the above spectra are very much identical and there is no significant difference in the shape or % transmittance of the peak. This preliminary study suggests that ovening of polyethylene MT10 grade (PSB0287/STD) material has not changed the structure of the processed material or degraded the polymer by the formation of carbonyl oxidation products.

Conclusion

All the three samples were analysed and all the three FTIR spectra are very much identical. This initial stage testing and analysis showed the ovening process (6hrs@65^{o}C) has not degraded the MT10 grade polyethylene.

5.3. INVESTIGATION OF CONTAMINATION ISSUES

As part of this KTP program various materials related issues were investigated and identified the root cause. Below mentioned is an example of tests carried out to identify the contamination in various filter parts.

Example 1- It was reported that a few batches of UDV 20 and UDV 50 filter media were contaminated with brown coloured stain. The aim of this study was to analyse the contaminated and non contaminated samples using Scanning Electron Microscope (SEM) and identify the chemical nature of the contaminant.

Following samples were analysed using a SEM at Microscopy and Analysis Suite, University of Bath

a) Dark stained sample
b) Light stained sample
c) Non stained sample.

(i) SEM Analysis

In scanning electron microscopy (SEM) an electron beam is scanned across a sample's surface. When the electrons strike the sample, a variety of signals are generated and it is the detection of specific signals which produces an image or a sample's elemental composition. The SEM is routinely used to generate high-resolution images of shapes of objects and to show variations in chemical compositions. Precise measurement of very small features and objects down to 50 nm in size can be accomplished using the SEM. Gedde (1995) has explained the working principle of SEM in his book “Polymer Physics”. The electrons that hit the surface of the specimen yield secondary electrons (used for the image), backscattered electrons (used for the image), Auger electrons (50- 2000eV) and X-ray radiation. The secondary electrons have relatively low energies less than 50eV

and they cannot escape from depths greater than 10nm in the specimen. The wavelength of the emitted X-ray is unique for a given element. An X-ray micro analyser attached to the SEM was used for detailed elemental analysis of the surface material.

Results

Figure 5.8 shows the SEM image of a single layer filter membrane at 10,000 magnifications. Figure 5.9, 5.10 and 5.11 shows the SEM images of uncontaminated, light contaminated and dark contaminated sample.

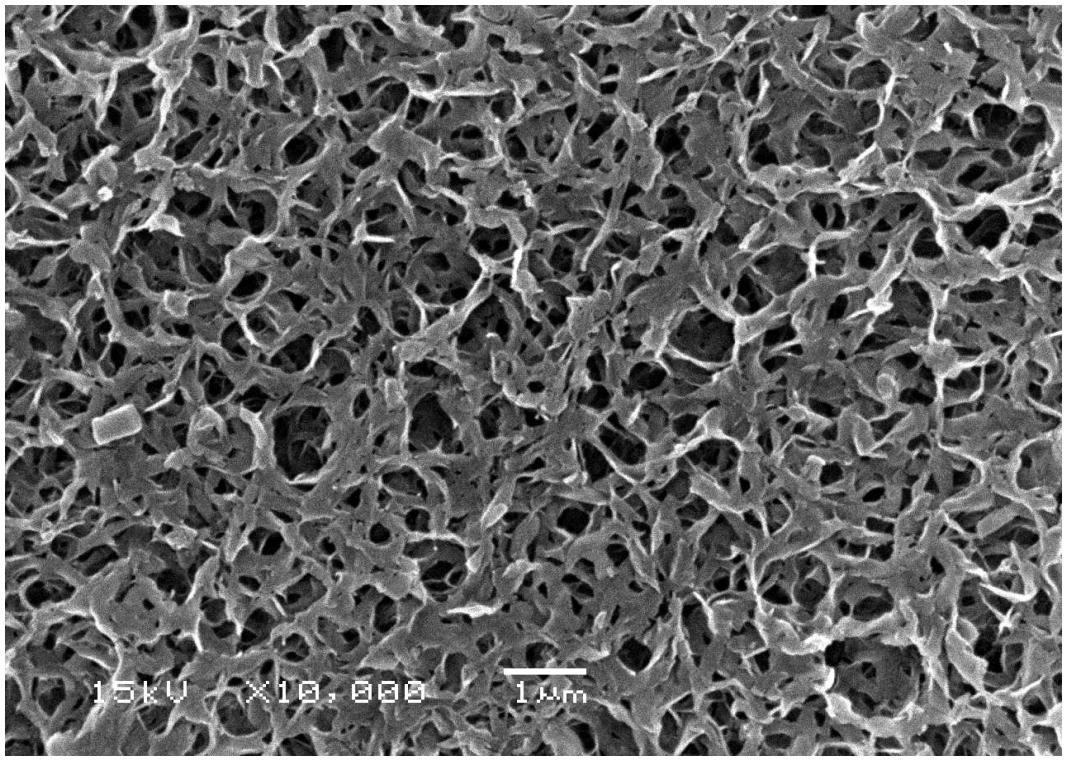


Figure 5.8- SEM image of single layer filter membrane

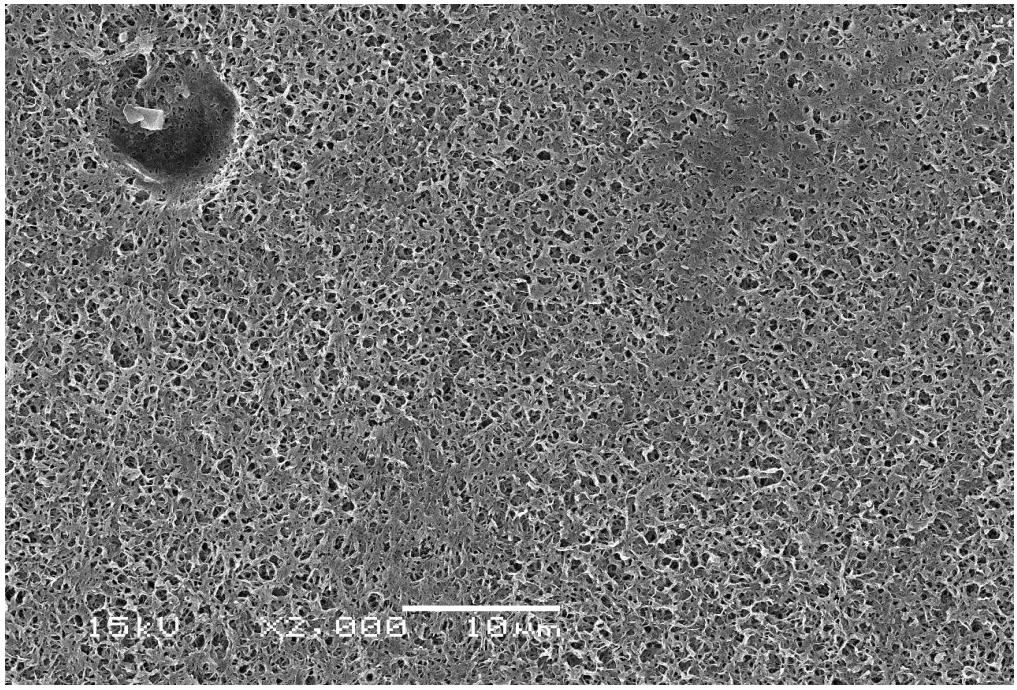


Figure 5.9 SEM image of uncontaminated sample

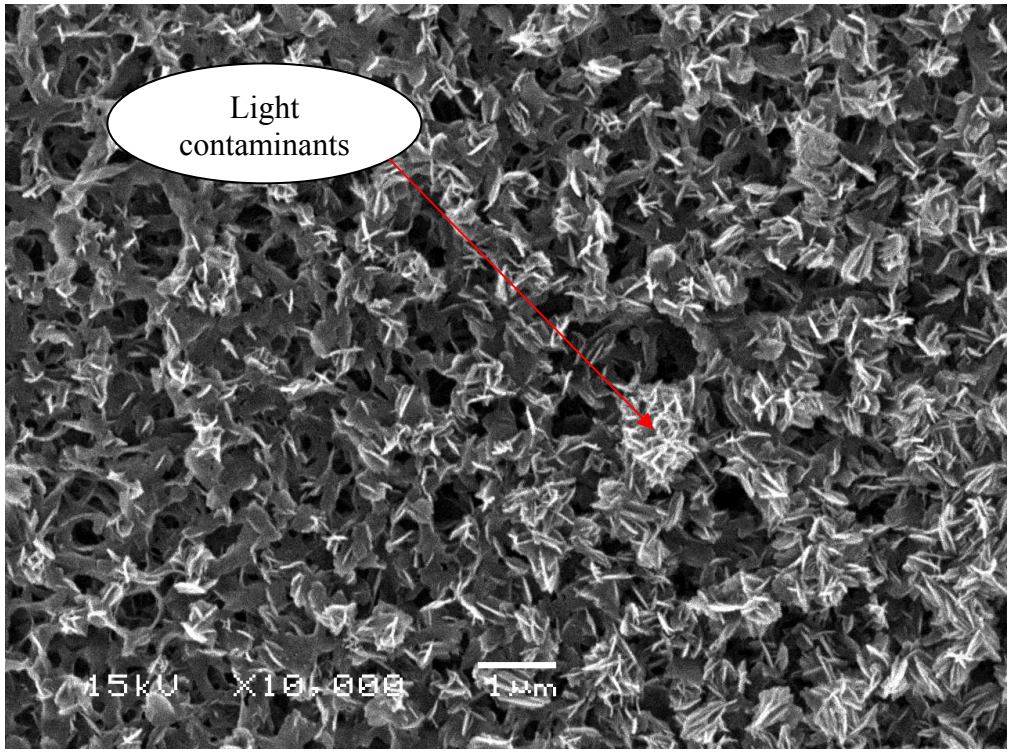


Figure 5.10 SEM image of light contaminated sample

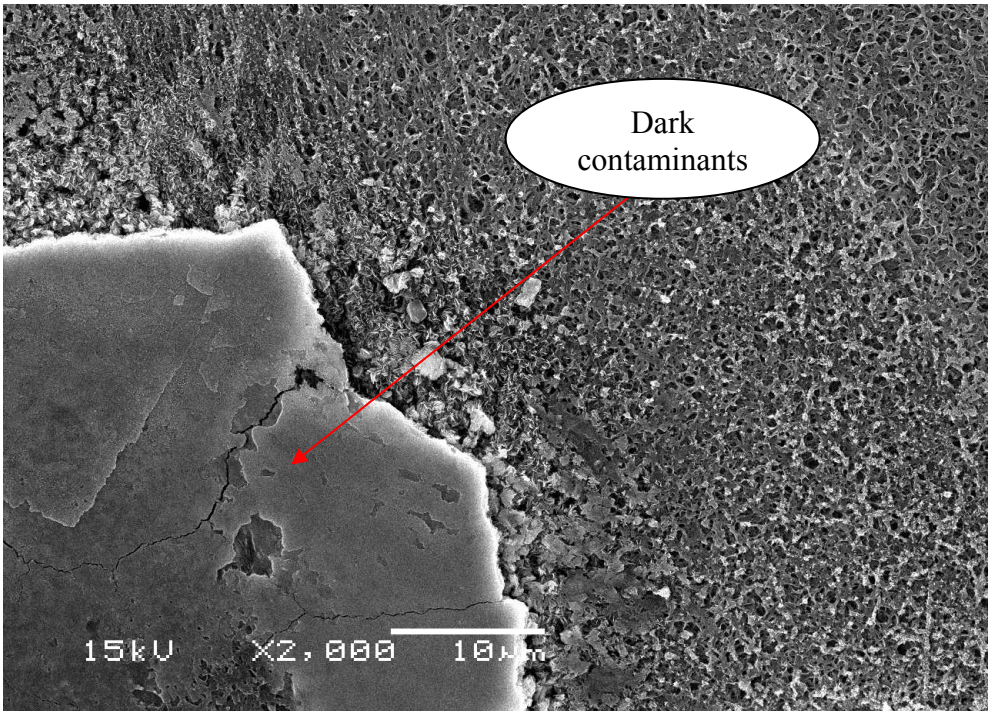


Figure 5.11 SEM image of dark contaminated sample

(ii) Elemental Analysis

Elemental analysis has been carried out with an X-ray micro-analyser to determine the elemental composition of the surface material. Figure 5.12, 5.13 and 5.14 shows the elemental analysis of uncontaminated filter media, contaminated light stain filter media and contaminated dark stain filter media.

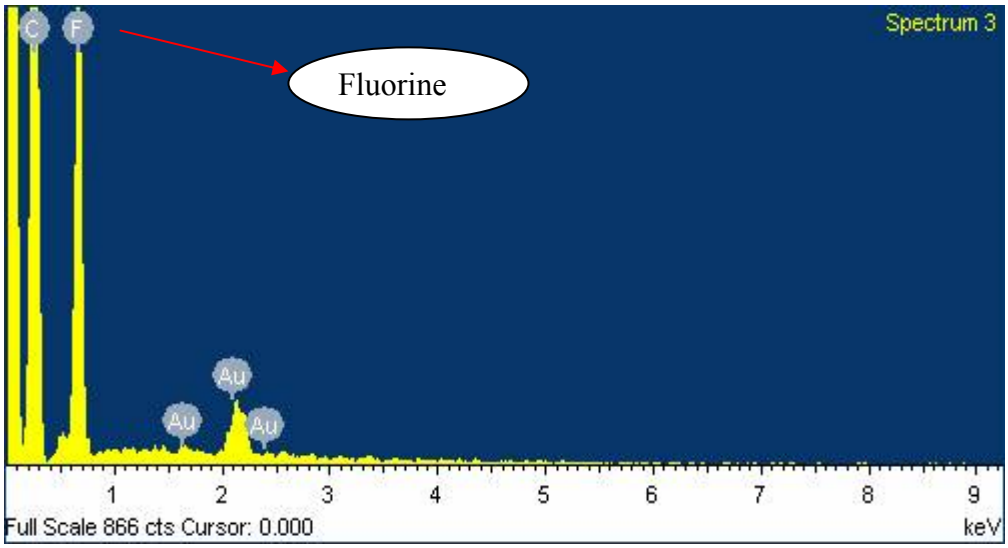


Figure 5.12 Elemental analysis of uncontaminated filter media

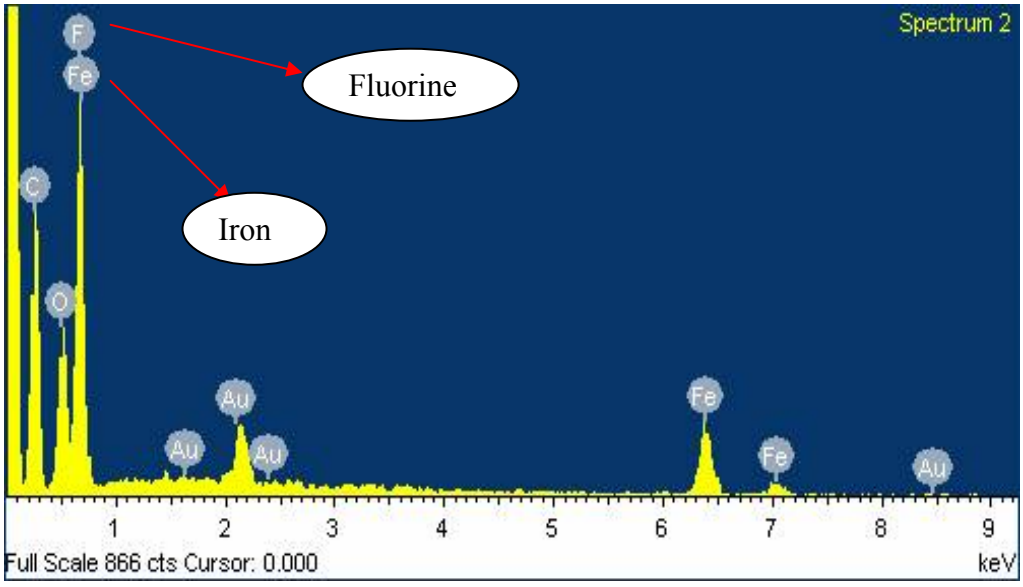


Figure 5.13 Elemental analyses of light stain filter media

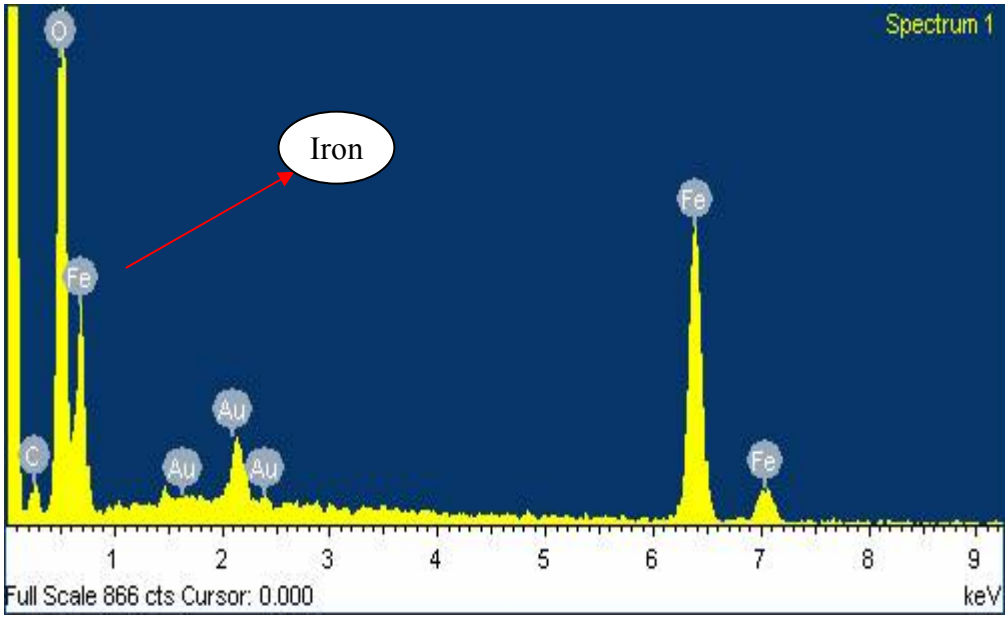


Figure 5.14 Elemental analysis of dark stain filter media

Discussion

The SEM image of the dark stain sample showed a fragment of foreign material (figure 5.11) on the surface of the filter media. Elemental analysis has been carried out on this foreign material and a high concentration of iron (Fe) particles was identified within the contaminant. The SEM image of the light stain sample (figure 5.10) shows the foreign material is spread and bonded on the surface of the filter

media. Elemental analysis shows the presence of iron particles and fluorine (F) on the surface of the media. Hence the filter media is made of fluorine based polymer and the contaminant is iron particles. The same tests were carried out on non contaminated samples and no presence of iron particles was observed. The brown colour was most likely due to the oxidation of iron particles and the formation of rust (iron oxide) on the surface of the filter media.

5.4. WELDING/END CAPPING ISSUES

Introduction

Pall Ilfracombe use a hotplate welding technique to weld filter components. It was noticed that while welding polypropylene components, strings were formed and because of cosmetic requirements these products could not be sent to customers. This affected the overall throughput of the welding process. A study was conducted to investigate the root cause of string/fibre formation during the hot plate welding of polypropylene material to propose an effective solution to prevent the problem happening again. Expected outcome from this study were a) A reduction in scrap rate b) Reduced lead time and c) Achievement of good quality weld.

Problem

Figure 5.15 shows a bad quality weld with strings formed at the interface. This string formation has resulted in cosmetic rejection of filter modules, loss of production time and increase in lead time

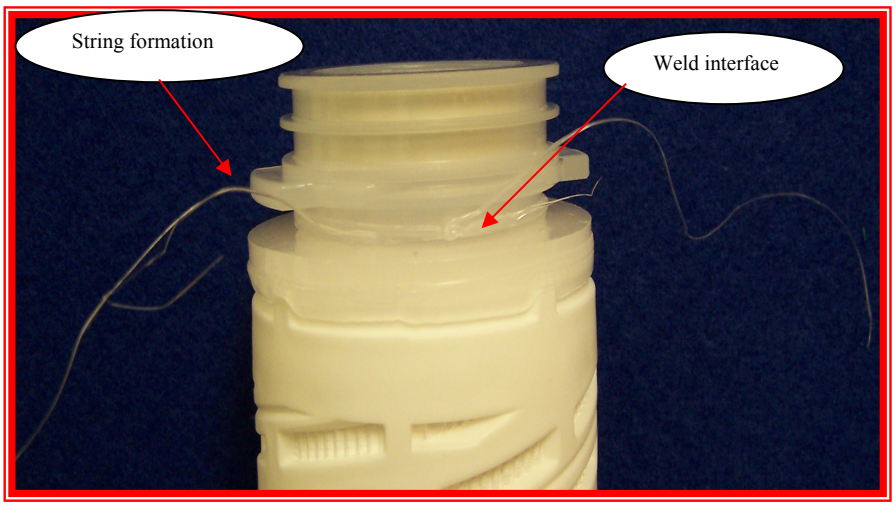


Figure 5.15- String formation at the weld interface

Root cause analysis

A cause and effect diagram or fishbone diagram has been used to identify the root cause of the stringing issue. This method can be used for cause identification once the definition of the problem has been established. Figure 5.16 shows the fish bone diagram prepared as part of a root cause analysis carried out to investigate the stringing issue.

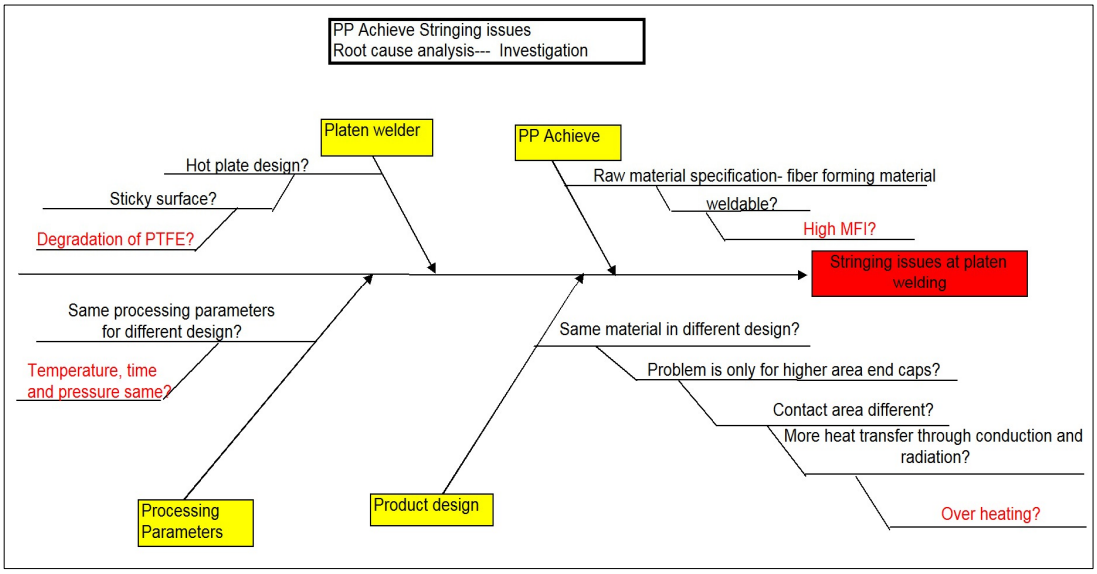


Figure 5.16 Fish bone diagram

Root cause analysis provided enough information about various potential causes of the problem. The results from the analysis concluded that the stringing problem could be due to one of the reasons below.

(i) Stickiness of the molten plastic on TEFLON film.
(ii) Non optimisation of welding parameters.
(iii) Material issues.
(iv) Over heating of weld platens

Following actions were taken to avoid the potential causes of the stringing problem.

(i) A design of experiment (DOE) was carried out to optimise the welding parameters.
(ii) Time, temperature and weld pressure were optimised to run the process at maximum through put.
(iii) Raw materials were quality checked using MFI, FTIR and DMTA before injection moulding to make sure materials were within Pall specification.
(iv) Regular temperature measurements were carried out to avoid over heating of weld platens.

The stringing problem was still evident after implementing all the above procedures. Several brainstorming sessions were carried out and a solution was found to stop the sticking of the molten plastic on the surface of the hot plate. A new coating system was sourced to apply on the surface of the hot plate to replace the TEFLON film. This coating system was found to be very durable and extremely non-stick. Figure 5.17 shows the new design with TEFLON coated metal plate as non-stick material.

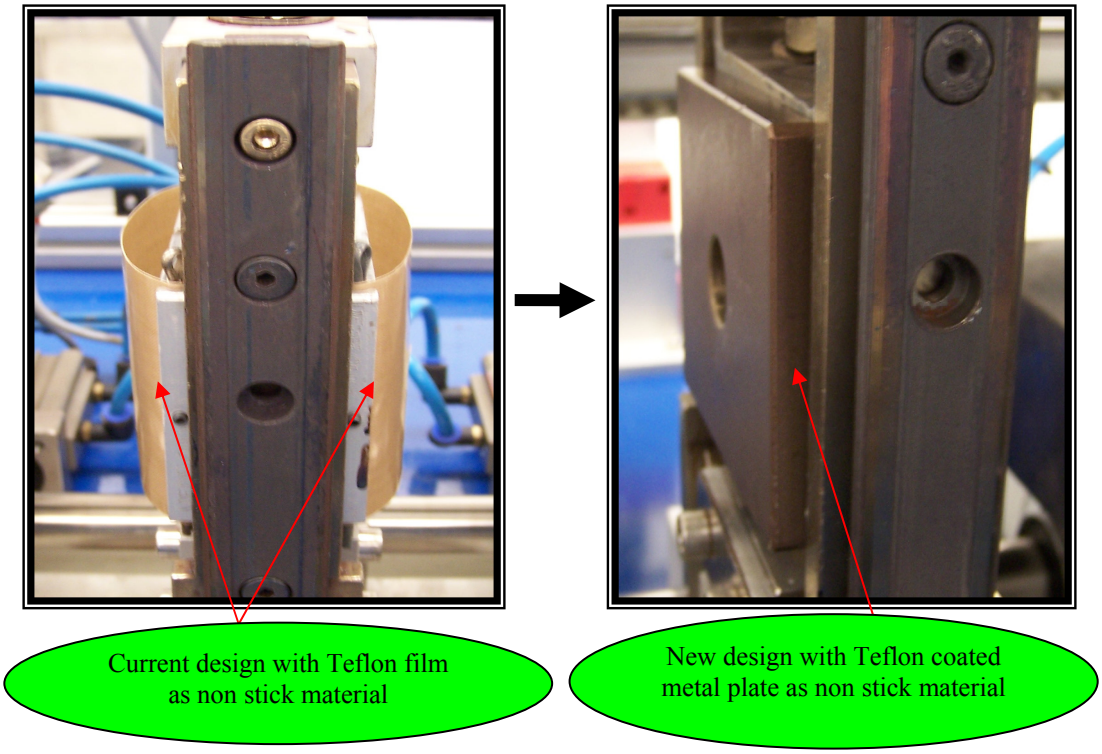


Figure 5.17 TEFLON coated metal plate as non-stick material for plastic welding

Processing parameters for welding different polymers were optimised after the installation of the new design PTFE coated metal plate. Figure 5.18 shows the time temperature curve for choosing the optimum weld parameters. The platen temperature to melt the part interface depends on the type of plastic being joined. Each thermoplastic has a characteristic melt time/temperature curve, and a weld can be produced at any temperature on the curve. Typically the highest possible temperature at the shortest time is selected to minimize cycle times.

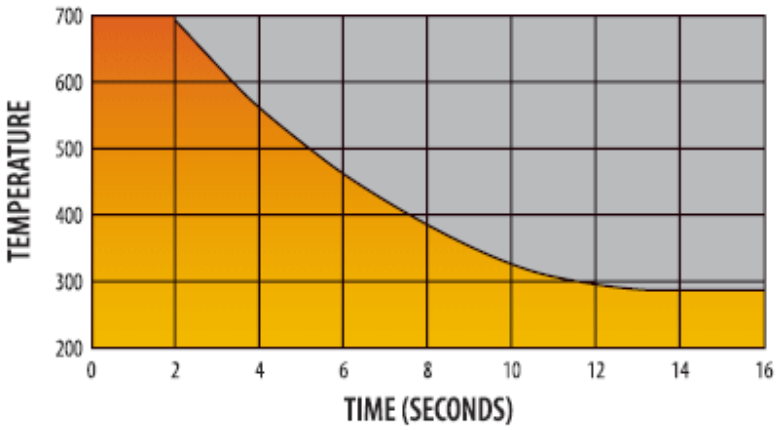


Figure 5.18 Time temperature curve (Taken from Forward Technology, 2010)

Following are the additional benefits of solving the stringing issues during the hot plate welding.

(i) Avoiding 5% of total weld rejects at Pall Ilfracombe
(ii) Insight into state of the art industrial polymers and manufacturing techniques
(iii) Identification of opportunities for future innovation in polymer engineering
(iv) Introduction of TEFLON coated metal plates in other production areas within Pall Ilfracombe for additional cost savings.

5.5. CHAPTER SUMMARY

This chapter has covered various polymer characterisation techniques and their applications within Pall Ilfracombe for the selection and quality assessment of materials to manufacture best quality filter systems. Several case studies including identification of batch to batch variation in polymer feed stock, investigation of contamination issues and welding / endcapping issues were explained with relevant examples in this chapter. Pall Ilfracombe has already benefited from its capability to characterise polymeric materials and assessment of materials related manufacturing issues. Batch to batch variation between polymer feedstock was still an issue and chapter 6 explains the successful introduction of a new quality assessment and evaluation method using identiPol-QA for final approval of manufactured products.

CHAPTER 6. IDENTIFICATION OF BATCH TO BATCH VARIATION IN POLYMER FEED STOCK USING identiPol-QA

6.1. INTRODUCTION

Before this KTP project there was a lack of ability to accurately profile materials for process set-up and ensure the smooth running of various filter manufacturing units within Pall Ilfracombe. This chapter explains the introduction of a method for quality control of thermoplastics for manufacturing industrial filters using an identiPol-QA thermo-mechanical analyser within Pall Ilfracombe and external suppliers. A detailed literature review of identiPol-QA and its functionalities was carried out and is described below.

6.2. REVIEW OF PREVIOUS RESEARCH

Different quality issues and their consequences on end products are explained in detail in Chapter 3 of this thesis. Plenty of research is in progress to develop equipment which can rapidly assess the quality of plastic parts. The importance of quality control systems for polymer production processes is discussed by Ohshima and Tanigaki, (2000), who explained that the quality of the polymer is affected not only by reactors operation conditions where polymers are synthesised but also by processing methods such as extrusion, injection moulding, drying, blending etc. Polymer properties are determined by low-order and high-order molecular structures. Ohshima and Tanigaki, (2000) state that "to provide the production plant with an enlarged capacity for product discrimination and flexibility, the polymer properties should be controlled on each molecular structure level in a consistent way throughout processing history from reactors to separation units, extruders, and to blending tanks". Measuring batch to batch variation of polymers due to difference in

low order and high-order molecular structure is a complex process and not all characterisation methods can be used for this determination. FTIR spectroscopy is a quick and easy method to check the quality and identification of polymeric material. But it is inappropriate to use this technique to study the batch to batch variation or mechanical properties of the material. The description of a quality control system and implementing a method for identifying batch to batch variation of polymers in an industrial environment is the main focus of this chapter.

Classification of polymers is briefly covered in section 2.3.1 of this thesis. The unique characteristics of polymers suit them for their end use application but in many cases these properties can degrade while passing through different stages of processing. Methods for determining the quality and consistency of a manufacturing process by assessing the quality of the final product are essential for the polymer manufacturing/ processing industries. A method to determine unknown polymers based on the thermomechanical characteristics of polymers was studied by Brereton *et al,* (2007). DMTA (section 4.3.1 of this thesis) can assess the change in molecular relaxation of a polymer after a force is applied during a temperature scan. The use of this technique for a rapid quality screening process was the main focus of their study.

DMTA is not a complicated instrument to operate but the interpretation of data requires materials expertise. Brereton *et al*, (2006) studied the possibility of modifying the DMTA using automated methods to group polymers by analysing the characteristic curves from each analysis. Chemometrics is the tool used for the extraction of information from the DMTA analysis and their study shows the combination of DMTA with chemometrics can be used as a powerful tool for polymer identification and quality control in a polymer production / manufacturing environment.

To understand the thermomechanical characteristics of polymers it is important to understand the different phase transitions in polymers. Substance can exist in three different states - solid, liquid and gas. A phase transition is simply the transition

from one phase to another involving changes in the arrangements of molecular structure and thermodynamic properties. In the solid state, polymers are classified into amorphous and semicrystalline based on the molecular arrangements. Tager, (1978) has reported that for crystalline and amorphous polymers there are two possible ways of passing from liquid state to solid state namely crystallisation and glass transition. Crystallisation can be described as a phase transition of the first order where there is a transition from a short range order to a long range order of molecules. But glass transition is the process of moving from a glassy state to a rubbery state with no change in phase. All polymers show glass transition behaviour when they change from the glassy state to the rubbery state and the temperature at which the transition occurs is called the glass transition temperature (Tg) (Ferry, 1980).

Figure 6.1 is a typical DMTA plot which shows that at the glass transition temperature (Tg), defined here as peak tan δ temperature, the storage modulus (E') decrease sharply and the tan δ which is the ratio of loss modulus (E") to storage modulus (E') passes through its peak value.

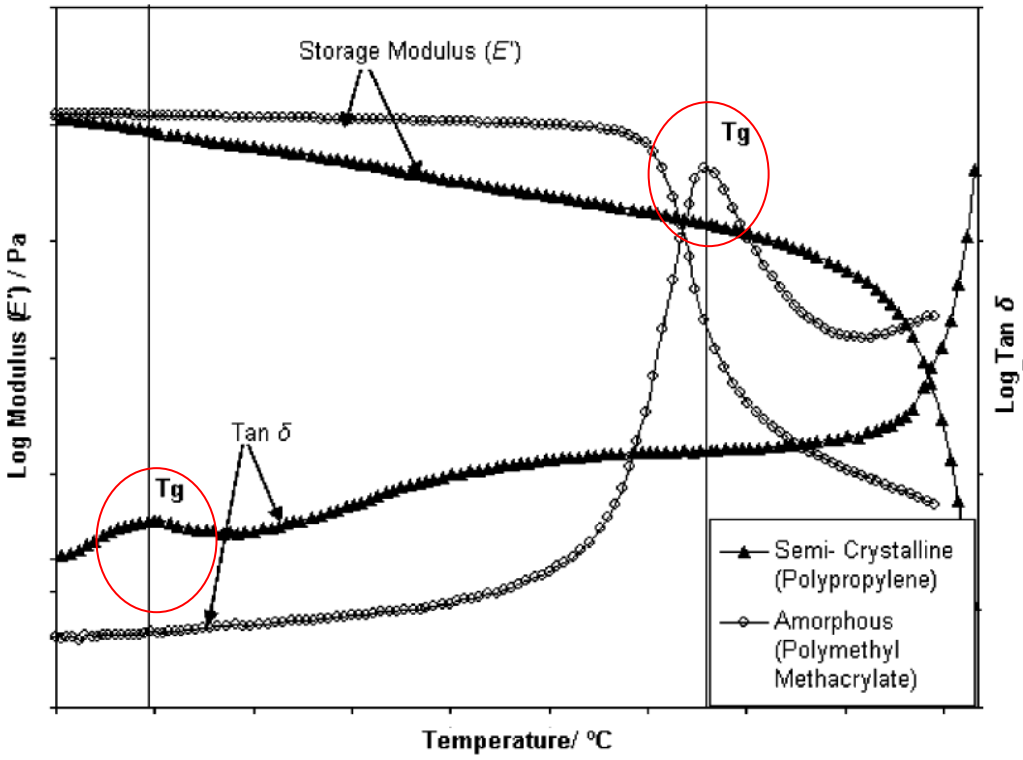


Figure 6.1: DMTA plot for a semicrystalline and amorphous polymer (Adapted from Brereton et al, 2006)

It is very clear from the above DMTA plot that for both semicrystalline and amorphous polymers, the peak of tan δ as a function of temperature indicates the difference in glass transition temperature of the polymer. Semicrystalline polymers show a small amplitude glass transition as the amorphous content within the polymer responsible for glass transition is less compared to fully amorphous polymers. Therefore the tan δ plot as a function of temperature can be used as a fingerprint for polymer identification because the ratio of energy dissipated to energy stored (Tan δ = E"/ E') indicates the molecular structure of the polymer and this is unique for each polymer (McCrum *et al*, 1976).

According to Wold (1995), chemometrics is "the art of extracting chemically relevant information from data produced in a chemical experiment". Using chemometrics a chemical problem can be structured to a form that can be expressed as a mathematical relationship. Brereton *et al* (2006) has published a paper on "pattern recognition for the analysis of polymeric materials" where different grades of amorphous and semicrystalline polymers were analysed by DMTA in combination with chemometrics. The authors demonstrated the applicability of chemometric techniques for polymer characterisation and identification. Figures 6.2 and 6.3 are two separate DMTA graphs which plot Tan δ against temperature for semicrytalline polymers (PP & LDPE) and fully amorphous polymers (PS and ABS).

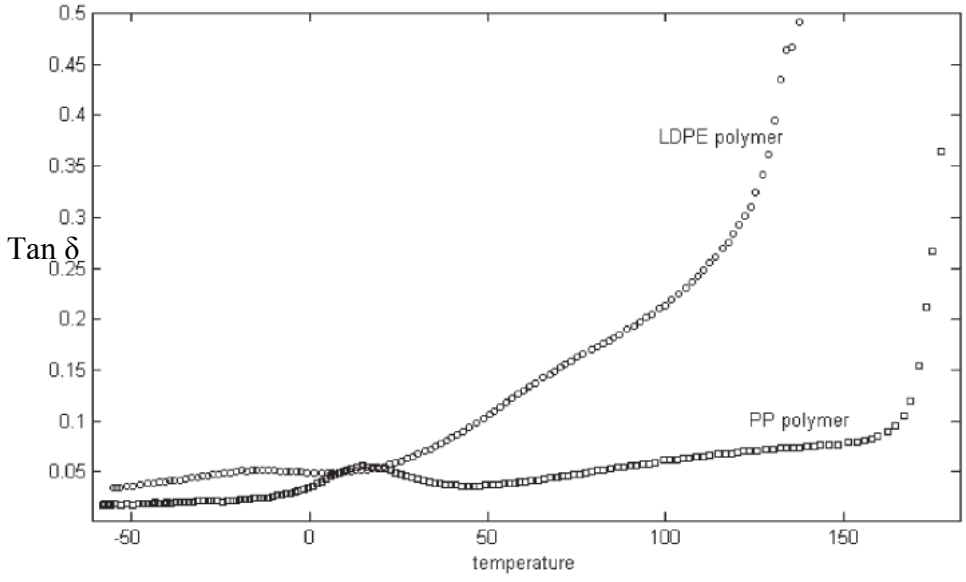


Figure 6.2: Tan δ plot of semicrystalline polymers – LDPE and PP {Adapted from Brereton et al, 2006}

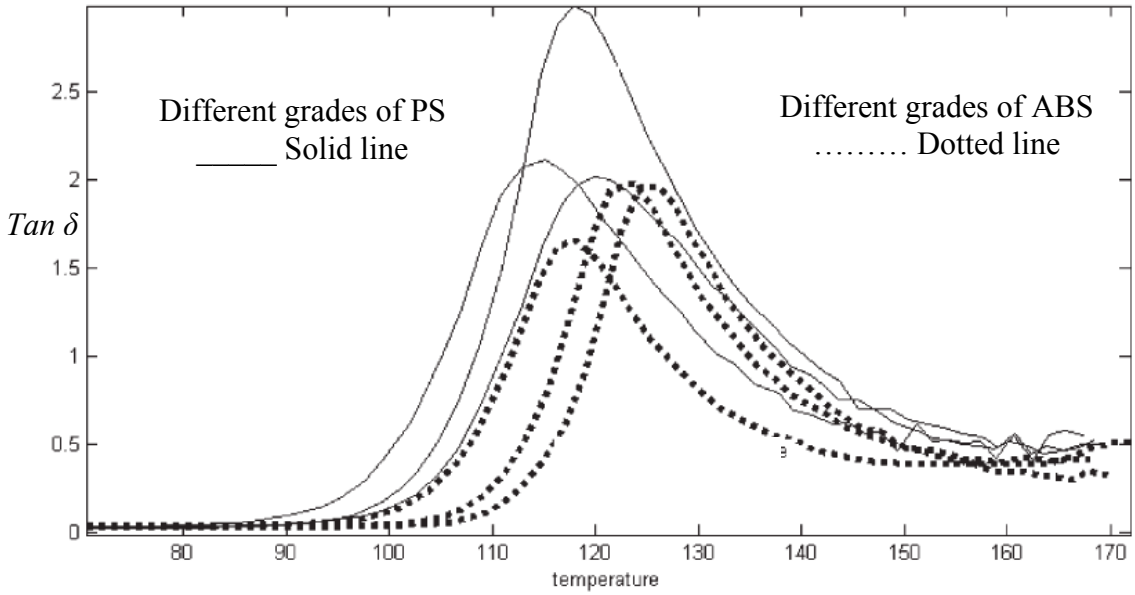


Figure 6.3: Tan δ plot of fully amorphous polymers – ABS and PS {Adapted from Brereton et al, 2006}

Principal Component Analysis (PCA) is a geometrical projection analogy used to convert correlated data models into a set of values of uncorrelated variables called principal components (Esbensen and Geladi, 2009). According to Brereton *et al* (2008), the most common approach in chemometrics for data visualisation is using Principal Component Analysis (PCA). It is reported in the same literature that "when using PCA as a graphical method for data visualisation, many different plots can be constructed once PCA has been performed". When there are many groups or grades of polymer samples for quality analysis PCA can be used to check the patterns in the data which reflect variation in chemical composition.

It is reported in the literature that relating two data matrices with the purpose of prediction or interpretation of data in chemometrics or statistics is a common problem (Langsrud and Naes, 2003). The score plot is one of the methods used for interpreting the relationship between values plotted in an X-Y form. The score plot in Figure: 6.4 shows that four groups of polymers investigated in a study by Brereton *et al*, (2006) are well distinguished and divided into sub groups based on different grades. The plot shows that both semicrystalline polymers PP and LDPE

can be easily distinguished from the amorphous polymers PS and ABS. The plot also shows the risks involved in classification of amorphous polymers if the difference between two grades of different amorphous polymers is less than the difference between two different grades of the same polymer. It is concluded in this study that the combination of dynamic mechanical thermal analysis and chemometrics has significant promise for polymer identification and characterisation.

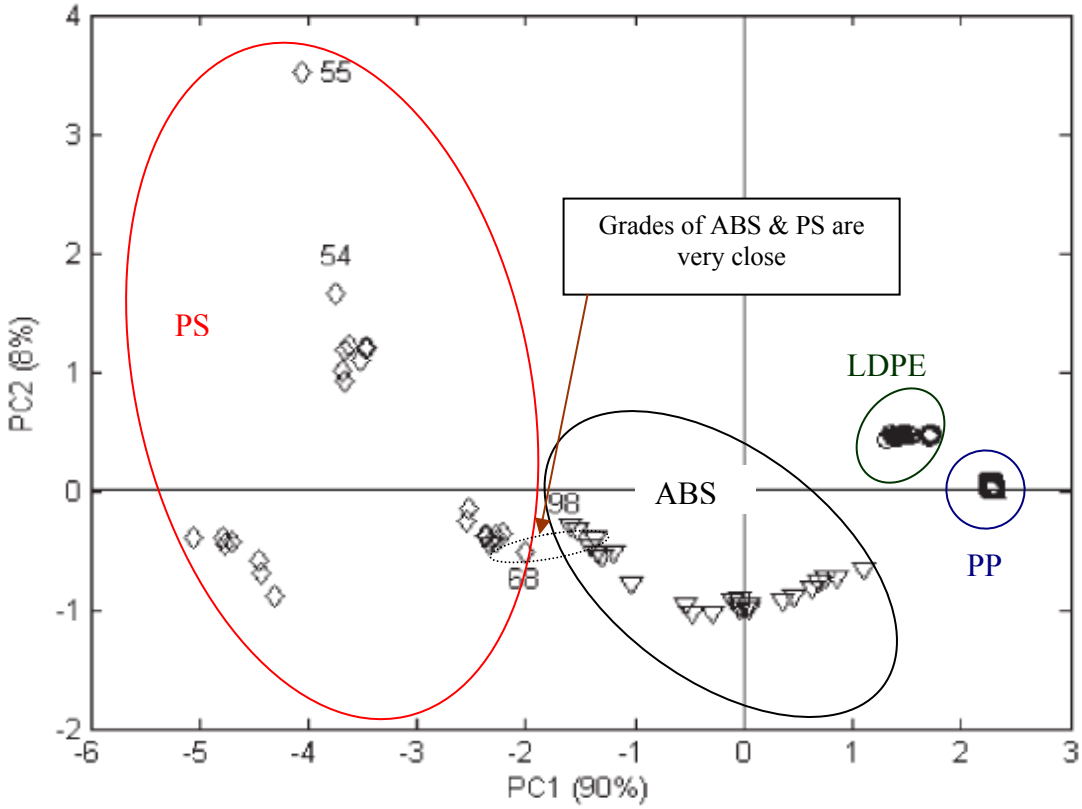


Figure 6.4: Score plot of whole set of PP, LDPE, PS and ABS specimens {Adapted from Brereton et al, 2006}

The data used in figure 6.4 came from the DMTA measurements for PP, LDPE, PS and ABS polymers. PC1 and PC2 are principal components and the scores are generated by the linear transformation of different set of variables like Tg, tan δ, storage modulus and Tm {Brereton *et al* 2006}.

6.3. identiPol- QA

The identiPol-QA unit is a rapid quality assurance device developed to check the quality of virtually any thermoplastic material. This equipment was developed jointly by the Chemometrics Department at Bristol University in the UK and Triton Technology Limited, UK. It is easy to interpret the output data from the identiPol QA and it offers an economical approach to assessing the quality of thermoplastics in an industrial environment. identiPol-QA uses technology which measures the thermo-mechanical properties of the polymer in a similar way to the

DMTA but in addition it gives a Quality Index Score (QIS) for the polymer. Figure 6.5 shows a typical identiPol-QA plot where QIS is plotted for a batch of polypropylene samples.

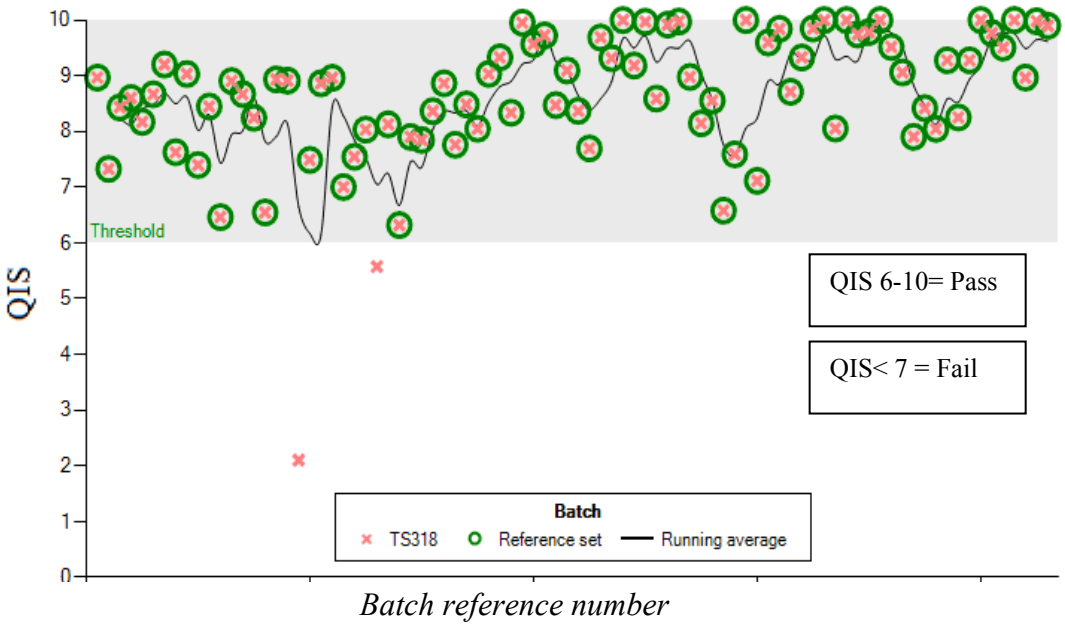


Figure 6.5- identiPol QA plot for polypropylene

Measuring batch to batch variation of polymers due to variation in low order and high-order molecular structure is a complex process and not all characterisation methods can be used for this determination. FTIR spectroscopy is a quick and easy method to check the quality and identification of polymeric material. But it is very

difficult to use this technique to study the batch to batch variation or solid properties of the material. identiPol-QA is a quick quality analysing device which can study batch to batch variation of any thermoplastic material.

Thermo-mechanical analysis of polymers and its use for polymer characterisation are explained in the literature (Li and Lambros, 2001, Badıa et al., 2009, Podczeck and Almeida, 2002). Thermo-mechanical degradation during polymer processing, contamination of the moulded parts and batch to batch variation of polymers can change the flow properties of the polymers, resulting in processing difficulties during final assembly. The identiPol QA thermo-mechanical analyser is a suitable device for the quality assessment of polymers providing clear values of the glass transition temperature (Tg), melting point (Tm), tan δ and Quality Index Score (QIS). The cost of identiPol is much less than other characterisation equipments like DMA, FTIR or DSC but the technical relevance is high. Figure 6.6 shows the positioning of identiPol in terms of cost and technical relevance.

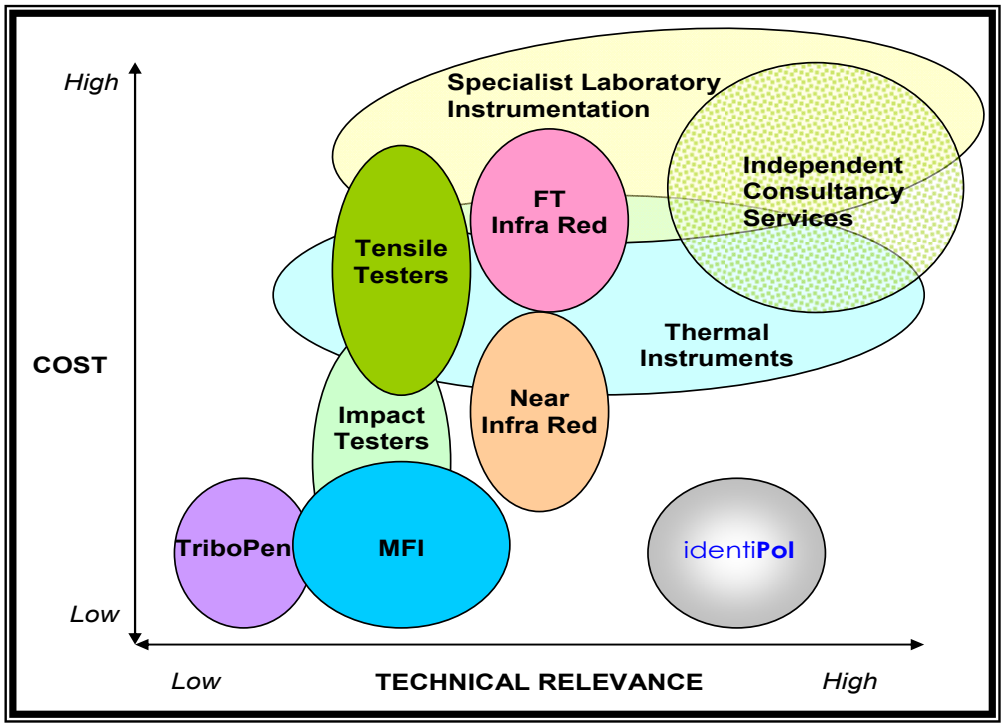


Figure 6.6- Positioning of identipol in terms of cost and technical relevance {Taken from Triton Technology Ltd, identiPol QA presentation January 2010}

6.3.1. identiPol-QA FUNCTIONALITY

identiPol-QA is a combination of DMTA and DSC. It measures the thermo-mechanical properties of the polymer such as storage modulus, tan δ and heat flow properties such as delta T similar to DSC (Ref: 4.4.1 of this thesis). At the end of the test, sample properties such as melting point (Tm) and Tg can be compared with those of reference polymers. identiPol QA software is developed based on chemometrics and the key properties of the polymer can be extracted from the thermomechanical data generated by the equipment. The identiPol-QA unit is trained by measuring at least ten fresh samples, which then constitutes a reference set. After creating the reference set for that particular grade of material, another batch of material can be compared against this reference set for QC purposes.

identiPol-QA equipment consists of two different sections called the “moulding section” and the “testing section”. The moulding section can be used for preparing samples for the test and the testing section is for sample analysis. There is a drive motor and displacement sensor mounted below the heater block in the testing section. Figure 6.7 and 6.8 shows different sections and schematics of the testing section of identiPol-QA equipment (Lukasiak and Duncan, 2010).

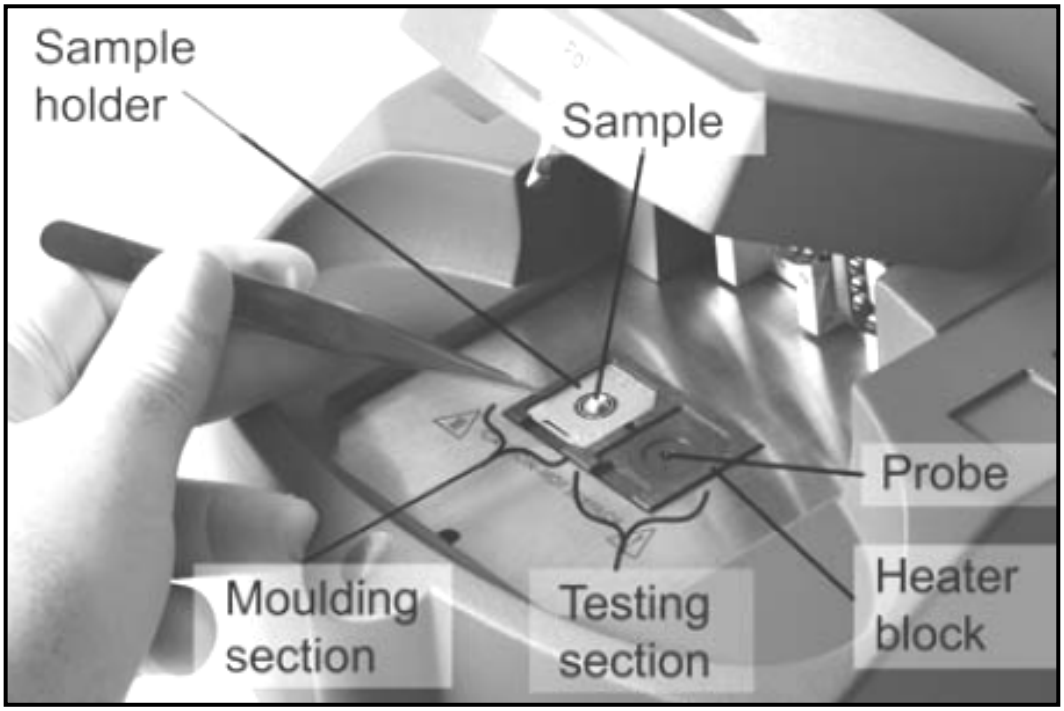


Figure 6.7: Different sections of identiPol-QA equipment (Adapted from Lukasiak and Duncan, 2010).

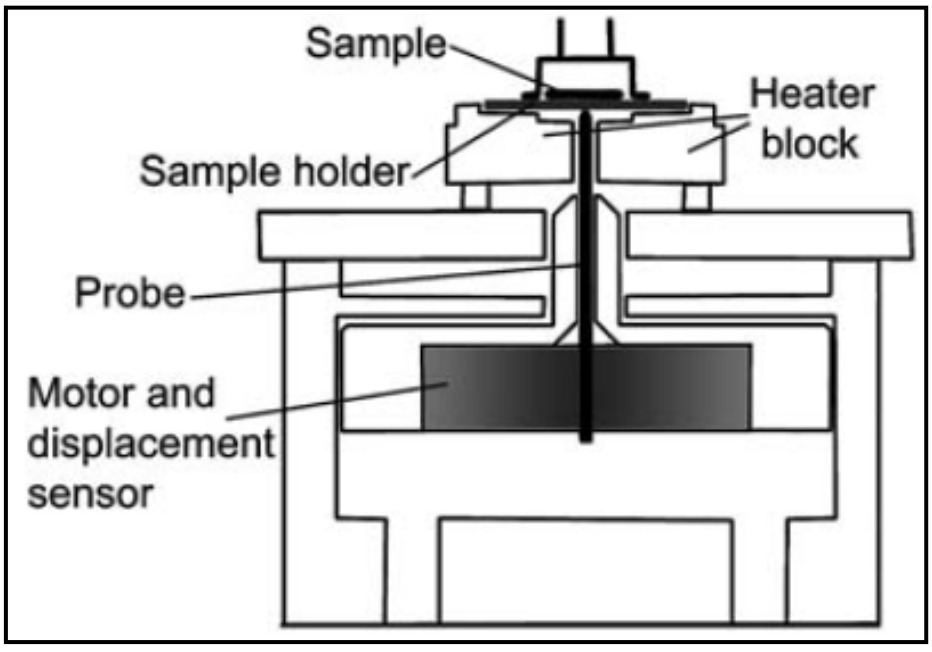


Figure 6.8: Schematic of the testing section of identiPol-QA (Adapted from Lukasiak and Duncan, 2010)

A test sample can be prepared by moulding 20 to 30 mg of polymers onto the sample holder on the moulding section of the identiPol-QA equipment. The polymer sample can be in the form of pellets or powders or a small part cut from a finished product. Once the sample is moulded on the holder, a composite of the sample and holder can be transferred to the analysis section. During the testing the composite can be heated at different heating rate. The motor applies a force by means of an actuator and software calculates the change in resistance to the applied force (Lukasiak and Duncan, 2010).

identiPol QA is controlled by software which runs the tests and analyses the data. Results of each test can be stored in a database which is created for that particular grade of material. identiPol-QA can be operated in three different modes a) Simple identification mode- which can be used to identify unknown material b) Batch consistency mode- which performs the quality assurance by measuring the QIS and c) Inter-batch comparison mode - which can be used to compare one batch of material against another from the same grade of material.

6.3.2. QUALITY INDEX SCORE (QIS)

QIS is a statistical representation of the output result from the identiPol-QA analysis. QIS is determined by measuring the thermo-mechanical properties of the material and comparing it against a previously established reference set. Since the equipment is measuring the thermo-mechanical property of the materials, it is the accurate way of monitoring the batch to batch variation in the process or in the material. QIS indicates the quality of the material and 7-10 indicates the samples are very similar and acceptable, 5-7 shows similarity, but with a difference, e.g. minor contamination and below 5 shows it is quite different.

6.4. IMPLEMENTATION OF identiPol-QA AT INJECTION MOULDERS

Pall Ilfracombe have purchased three identiPol-QA instruments for implementing a new quality control procedure within external suppliers of injection moulded filter components. I have worked with Triton Technologies to install the equipment at three external injection moulded part suppliers and trained the operators. A database was created with reference data for different grades of polypropylene, polyester and nylon polymers. The aim was to enable suppliers to check the quality of incoming raw materials before use in production, thereby introducing a quality control procedure to meet Pall specifications. As well as variations in the polymer feedstock, the property of the moulded parts can depend on the moulding parameters. Thermal degradation can happen to the polymer if the processing temperature is too high or the mould cooling temperature is not accurate. Suppliers were trained to use the identiPol unit to assess the quality of the moulded parts before they were sent to Pall Ilfracombe for filter assembly. Figure 6.9 shows a reference set created for a poly-butylene terepthalate (PBT) polyester material.

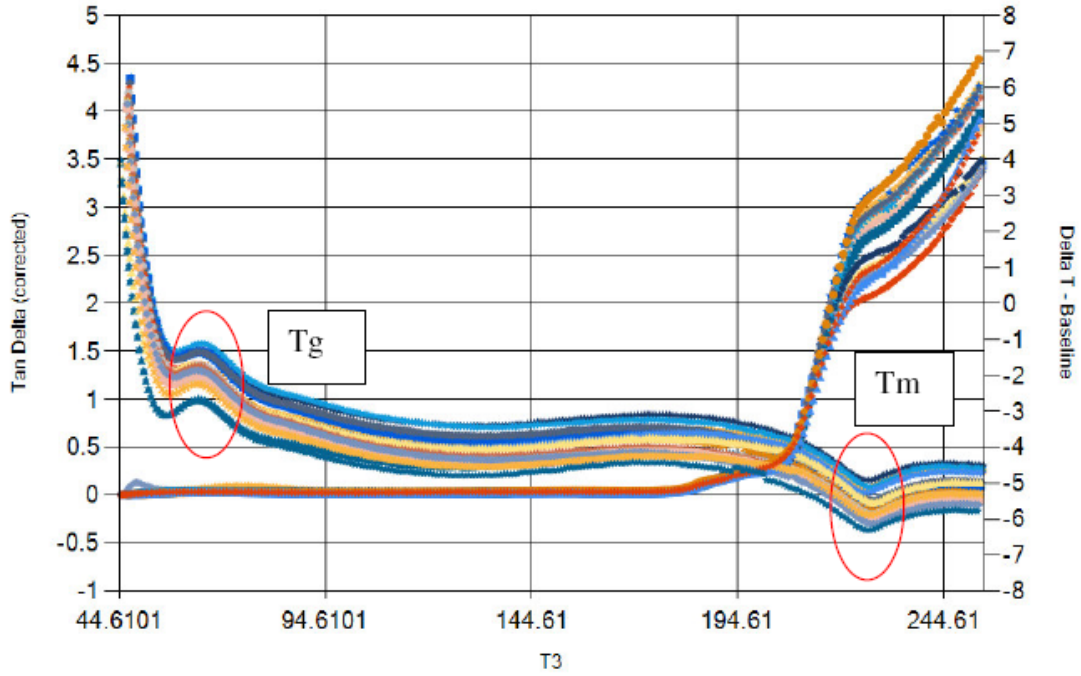


Figure 6.9: Identipol reference data for PBT (Tan Delta and Delta T vs. temperature).

Detailed information about the visco-elastic properties and thermal characteristics of the polymer is revealed by plotting Tan Delta and Delta T-Baseline against Temperature. Delta T- Baseline is a base line corrected Delta T which reflects the energy required to change the material as it is heated. As explained in section 4.1 of this chapter, tan delta is a measure of the mechanical damping properties of the polymer. The glass transition is the temperature at which the polymer changes from a glassy state into a rubbery state, characterised by a peak in the Tan Delta graph. The melting point is the temperature at which a semi-crystalline polymer changes from a solid to a liquid state and is characterised by a trough in the tan delta graph.

During the identiPol test, data is gathered from the instrument and values are stored in a data channel. IdentiPol QA software uses these data and generates a QIS by comparing it against a set of data. This set of data is called the reference set, created for each grade of material and is used to compare all future samples of a particular grade. A new batch of PBT was tested against the created reference set and Figure 6.10 shows the change in tan δ and delta T characteristics. The tan δ peak has reduced and the there is a shift in melting point as clearly evident from the delta T graph. There are batch to batch variations within the polymer and the identiPol unit has proved to be a very useful tool for the quality assessment of incoming raw materials.

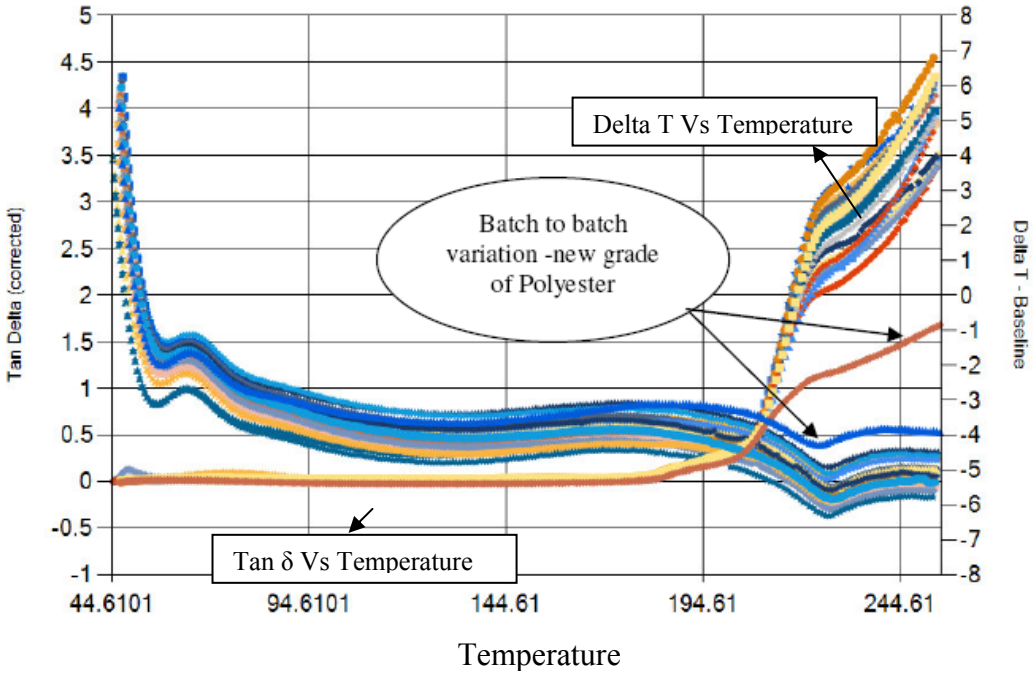


Figure 6.10: identification of batch to batch variation in polyester (PBT)

Figure 6.11 is a flow chart which illustrates various steps in the implementation of quality control procedures using identiPol-QA within Pall Ilfracombe and external suppliers.

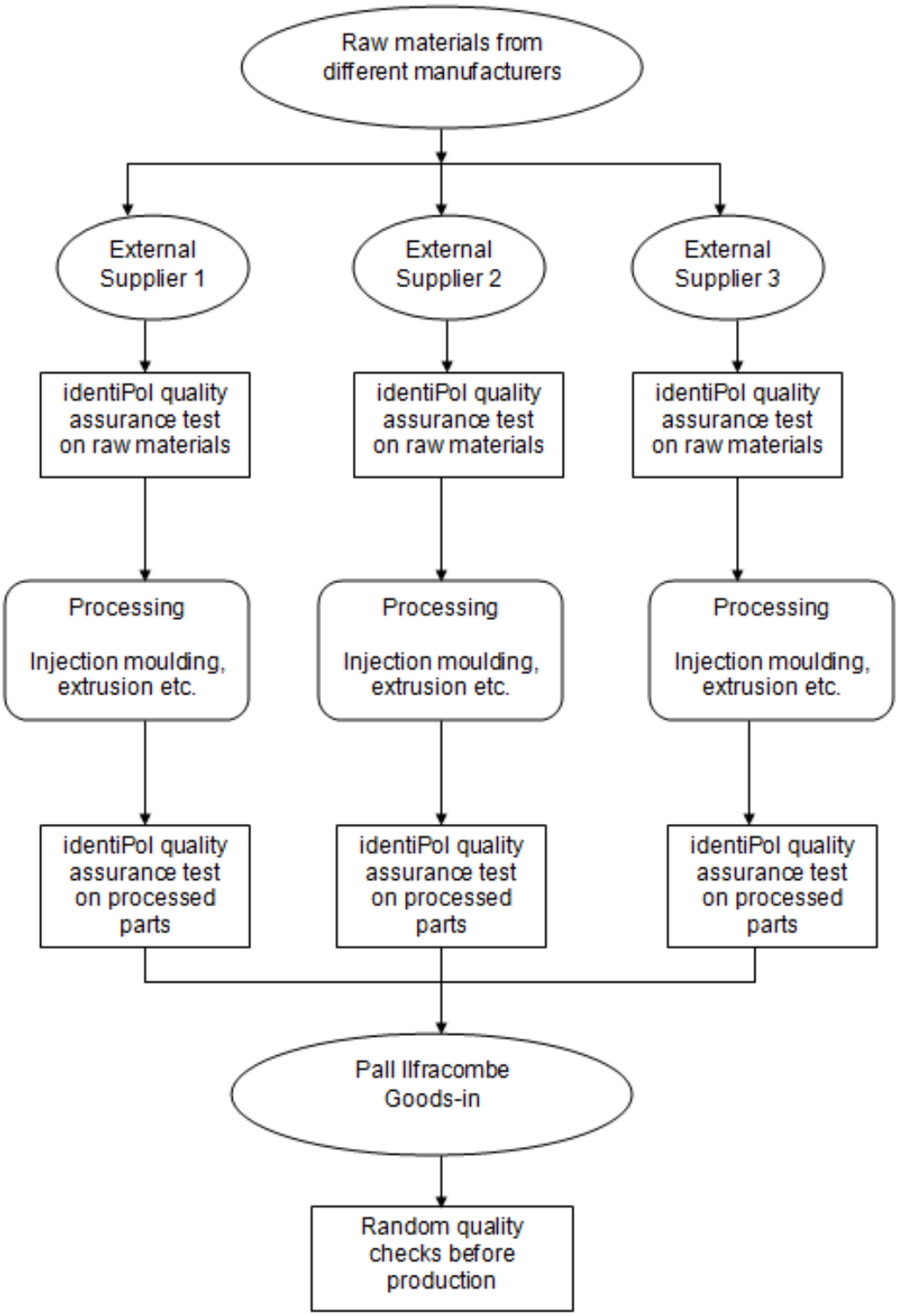


Figure 6.11: Process flow for quality control on raw materials and processed parts before filter manufacturing

6.5. CASE STUDY-1 [BATCH TO BATCH COMPARISON OF PP BE60 (OLD SUPPLIER VS NEW SUPPLIER)]

6.5.1. INTRODUCTION

Two batches of polypropylene extruded samples were received for batch comparison. Both samples looked to be very identical and have received from two different suppliers. PP BE60 received from the new supplier behaved differently during the processing trials. The aim of this study was to check if there is any batch to batch variation between two samples before considering the polymer from the new supplier for manufacturing the filter module.

Sample details

a) PP-BE60 – Old Supplier
b) PP-BE60 -- New Supplier

6.5.2. identiPol-QA TEST

IdentiPol-QA test was performed on PP-BE60 from the old supplier and the new supplier. Figure 6.12 shows the changes in stiffness and tan δ for both polymers when tested at a heating rate of 20°C per minute.

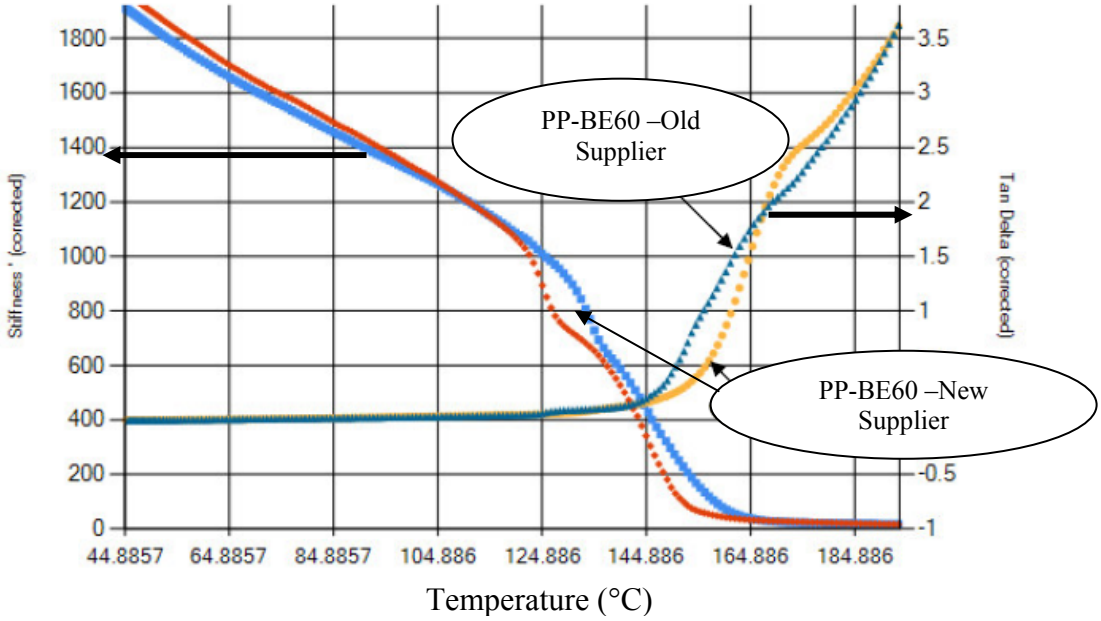


Figure: 6.12: identiPol-QA results- stiffness and tan delta Vs temperature

The test result shows within the temperature range 115°C to 164°C, the PP-BE60 grade from the new supplier is stiffer than the old grade. To confirm the melting point of both grades of polypropylene, a DSC analysis was carried out using an STA 6000 unit.

6.5.3. DSC ANALYSIS

Figure 6.13 and 6.14 shows the DSC graphs generated using the STA6000, which indicate the heat flow as a function of temperature. DSC analysis shows PP BE60 old grade has two melting peaks, peak one corresponds to temperature 152°C and peak two corresponds to temperature 164°C. This could be due to the presence of another low molecular weight polypropylene present in the base polymer or PP BE60 could be a copolymer. PP BE60 new grade DSC graph shows a single sharp peak at corresponds to 167°C which indicates the melting point. By comparing the above two graphs it is very clear that new grade polypropylene (PPBE 60 new grade) is different from the old grade (PPBE 60 old grade).

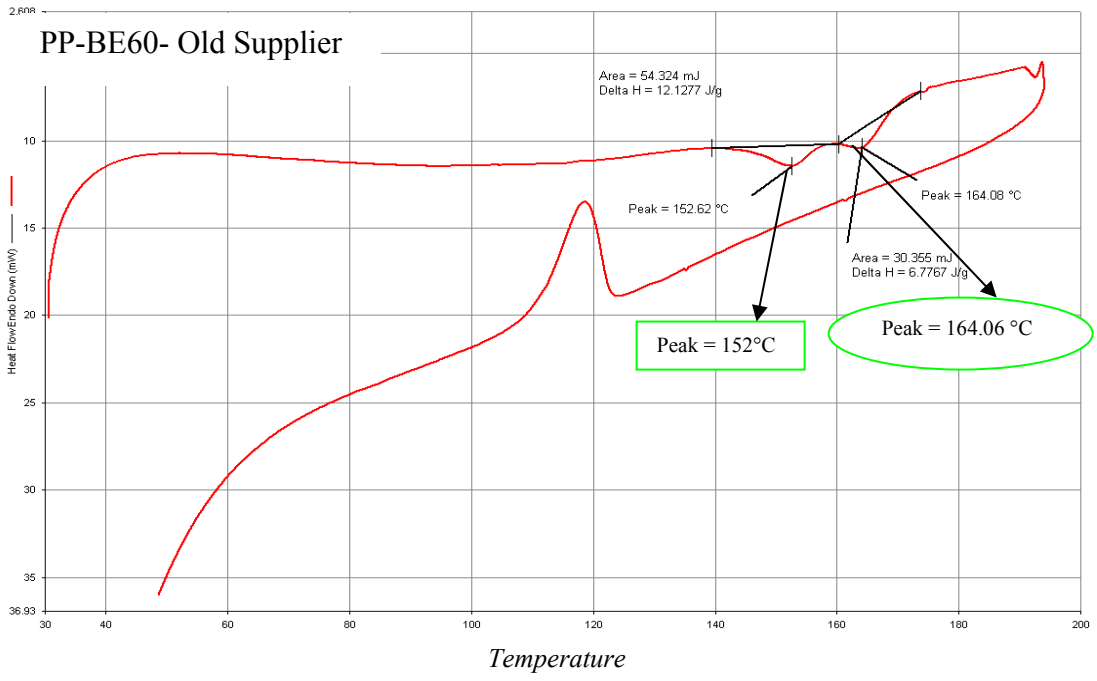


Figure 6.13: DSC graph of PP BE60 from old supplier

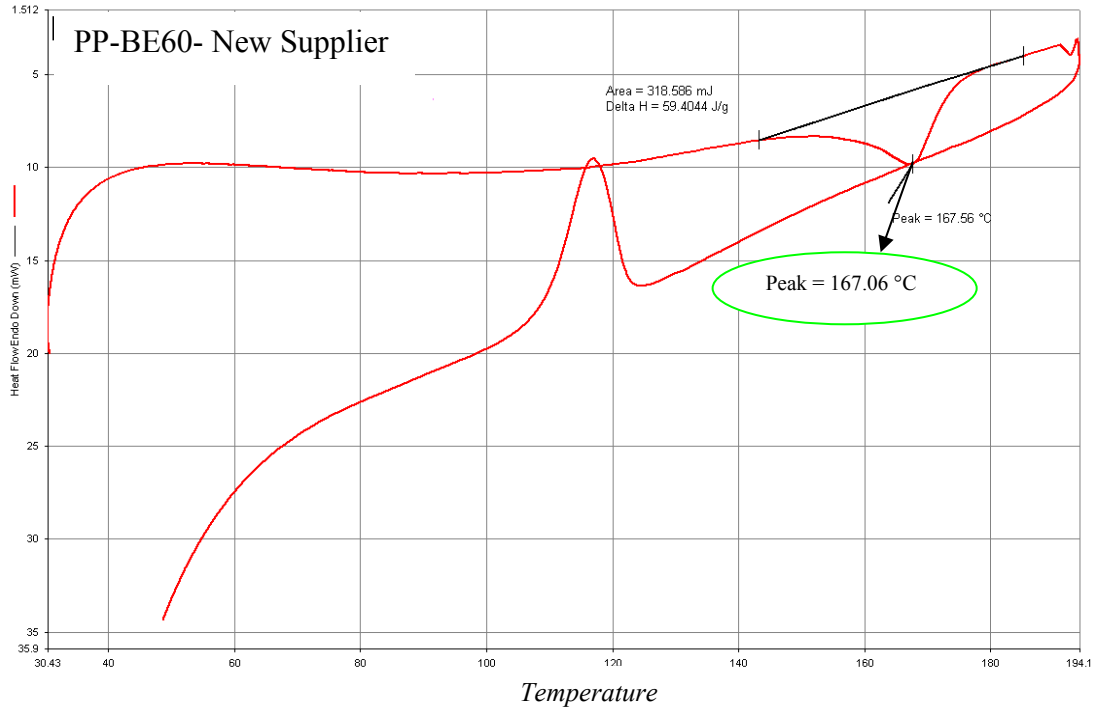


Figure 6.14: DSC graph of PP BE60 from new supplier

DSC analysis shows PP BE60 from the old supplier has two melting peaks, peak one corresponds to temperature 152°C and peak two corresponds to temperature 164°C. This could be due to the presence of another low molecular weight polypropylene present in the base polymer or the polymer from the old supplier could be a copolymer. PP BE60 new grade DSC graph shows a sharp peak corresponds to 167°C which indicates the melting point. By comparing the above two graphs it is very clear that new polypropylene (PP-BE60-New Supplier) is different from the old grade, so there could be processing problems associated with the welding of filter assemblies.

6.6. CASE STUDY 2- ENDCAPPING ISSUE

Problem: It was reported that a full batch of filters assembled in one of the shifts were failed during the end cap leak test.

Endcapping machine set conditions were checked and no problems were identified. Samples were collected from the good and failed batch and tested using FTIR to see if there were any differences in chemical characteristics. Figure 5.15 & 5.16 shows the FTIR spectrums of good and bad end caps and indicated no difference in the transmittance peak. It was concluded that both end caps are made of polypropylene material.

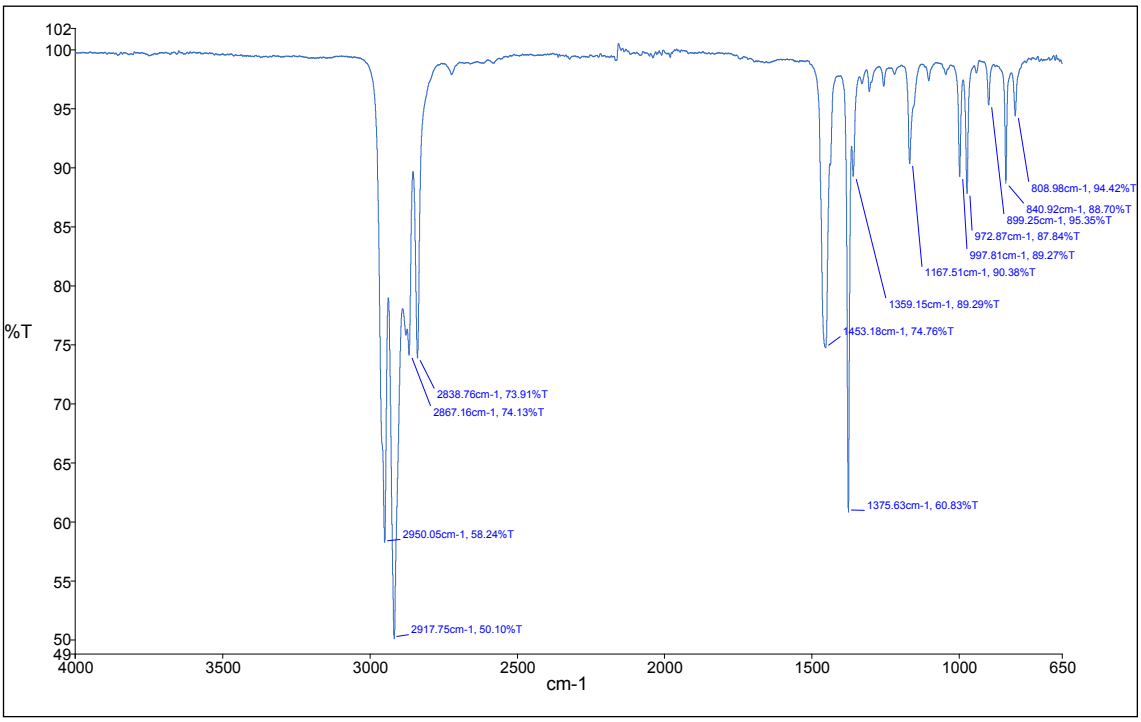


Figure 6.15: FTIR spectrum of good end cap

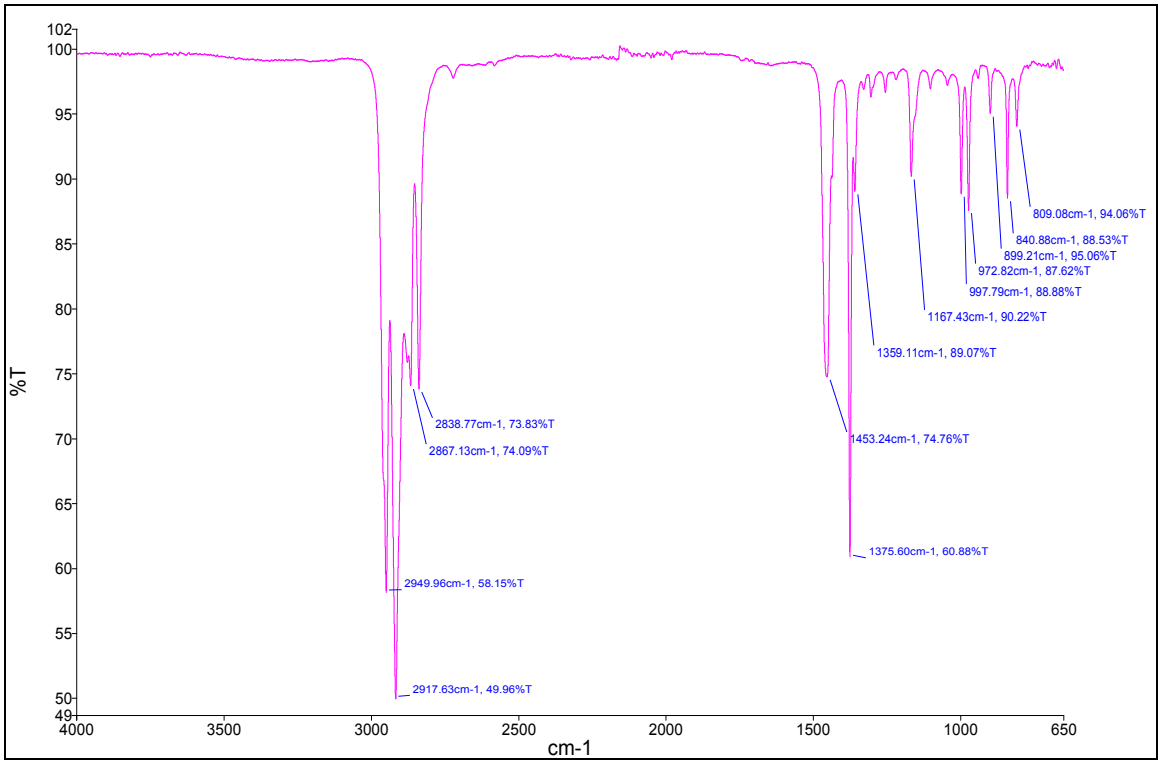


Figure 6.16: FTIR spectrum of bad end cap

Samples were further tested using identiPol-QA to study if there were any batch to batch variations between the good and the bad end cap. Using identiPol – QA a new reference set was created by testing nine samples from the good end cap. The quality of the reference set was confirmed by testing the tenth sample and confirmed with a QIS of 10. Figure 6.17 shows the QIS chart generated using samples from the good end cap.

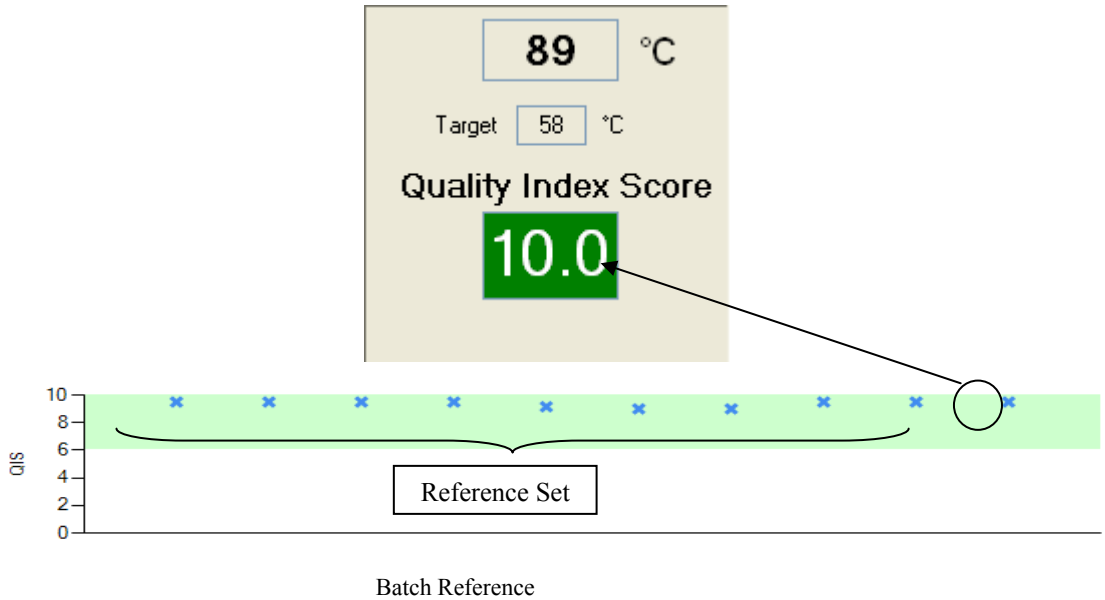


Figure 6.17: QIS plot

To evaluate if there was any batch to batch variation between the good and the bad end cap, a sample from the bad end cap was tested against the newly created reference set. Figure 6.18 shows the sample from the bad end cap gave a QIS of 0.9 which indicates there are significant differences between the thermo-mechanical characteristics of both end caps.

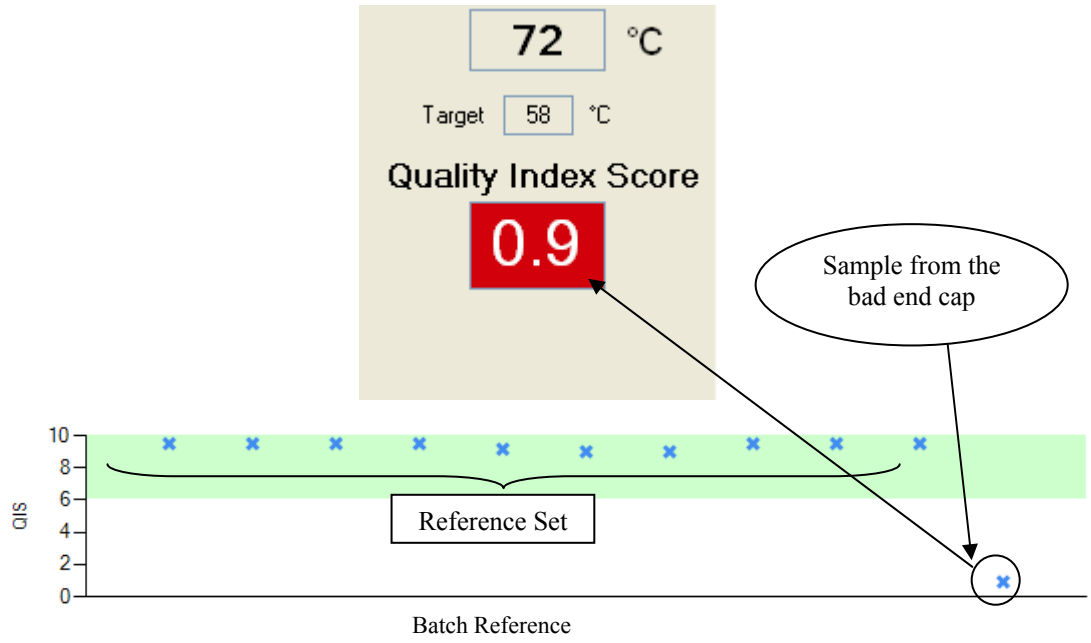


Figure 6.18: QIS plot {Good end cap Vs bad end cap}

A delta T- baseline / stiffness Vs temperature graph was plotted using identiPol-QA software and Figure 6.19 shows there is 10° C difference in melting point between the good and the bad end cap. Also the stiffness Vs temperature graph shows the bad end caps are stiffer than the good end cap at temperature above 115°C.

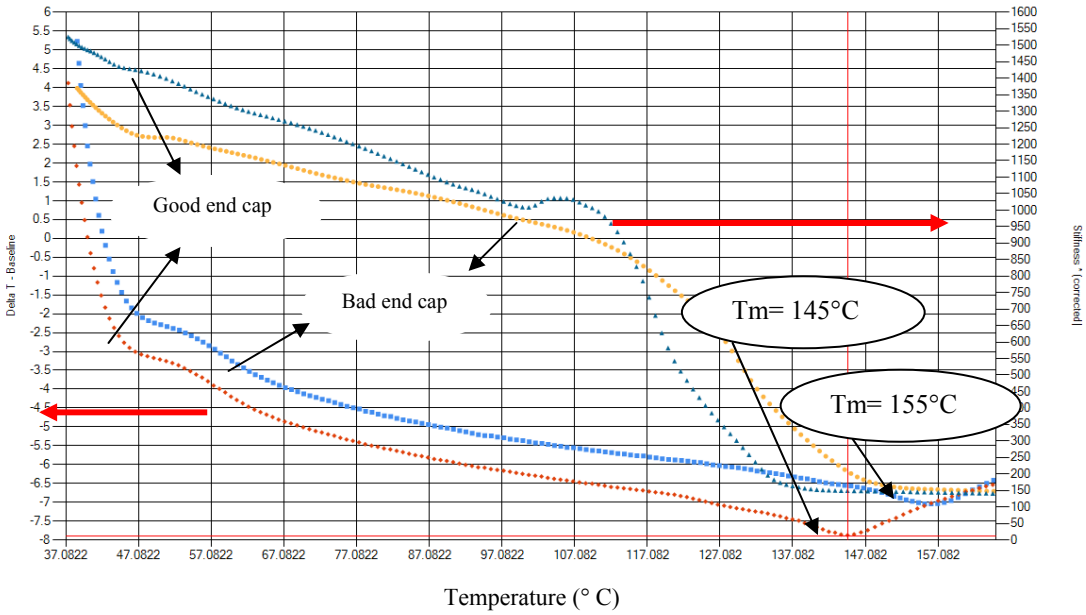


Figure 6.19: identiPol graph – good end cap Vs bad end cap

An MFI test was also carried out to check the flow properties of the good and the bad end caps. Table below shows the MFI of both samples are significantly different and this explains why the melt viscosity of good end caps was lower than the bad end caps.

Table 6.1: MFI test results

Sample	**MFI (gms/10min) 230°C/ 2.16 kg**
Good end cap	26
Bad end cap	11

Conclusion

The above test results concluded that the wrong grade end caps were used for making the filter modules and hence the reason for the endcap leak test failure. IdentiPol-QA was found to be a very reliable and fast test method to identify batch to batch variation

within polymer feed stock. It was concluded that due to the poor flow properties of low MFI grade material, the end cap wasn't melting enough at the set temperature to flow and form a good seal between the media and the end cap during the assembly process. QC procedures were implemented to avoid similar issues happen in the future.

6.7. CHAPTER SUMMARY

Pall Ilfracombe has introduced procedures for quality control of thermoplastics for industrial filters using identiPol QA thermo-mechanical analysis. The basic principle of identipol QA was covered in this chapter and it can be concluded that the combination of dynamic mechanical thermal analysis and chemometrics have significant promise for polymer identification and characterisation. A benchmark has been created for each grade of polymer and a QC procedure has been established on the premises of three suppliers who manufacture moulded components for Pall Ilfracombe. The author collaborated with Triton Technologies to install the equipment at three injection moulded part suppliers and trained the operators to measure QIS score. QIS is a statistical representation of the output result from the identiPol-QA analysis and this is determined by measuring the thermo-mechanical properties of the material and comparing it against a previously established reference-set. This chapter also covered a case study where identiPol-QA was used to study the batch to batch variation of polypropylene BE 60 between two suppliers. There is a potential chance for a roll out program to introduce this QC procedure across all manufacturing units of Pall Corporation globally.

CHAPTER 7. PLASTIC WELD REDUCTION- A SIX SIGMA APPROACH

7.1. INTRODUCTION

This chapter explains the importance of Six Sigma methodologies for making manufacturing process improvements within Pall Ilfracombe. Finding solutions for a temperature non-uniformity problem on a non-contact welding machine by using the Six Sigma process is the main focus of this chapter.

7.2. REVIEW OF PREVIOUS RESEARCH

Six Sigma (σ) is a methodology which aims to restrict variation in production quality to +/- 3 standard deviation about a target quality mean (Markarian, 2004). The approach of Six Sigma is to create a quality standard in a process with the chance of only 3.4 defects per million opportunities (DPMO). Figure 7.1 is a schematic representation of Six Sigma process.

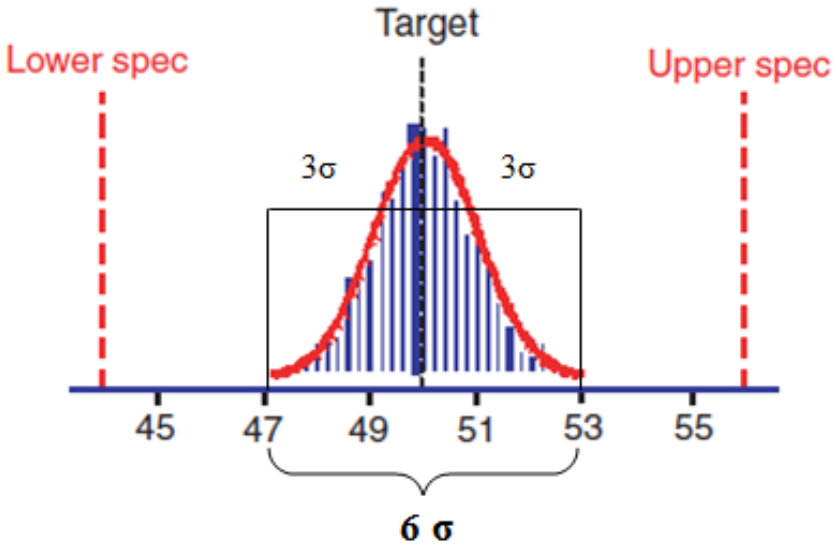


Figure 7.1: Six Sigma process {Adapted from What is Six Sigma, 2004)

Many production industries are combining Six Sigma and Lean Manufacturing processes to gain the benefit of both. Lean manufacturing is traditionally used as a method to eliminate waste and reduce inventory. According to Smith B, managing director at the Time Based Management (TMB) (Markarian, 2004), "Lean manufacturing tools are extremely important in chemical and plastics industries for reduction in set-up time and Total Productive Maintenance (TPM)".

7.2.1. SELECTION OF PROJECTS FOR SIX SIGMA

There are a few research papers on the importance of the selection of right project for the Six Sigma project for better results. According to Padhy and Sahu (2011), the most effective business transformational initiative in recent times is the implementation of Six Sigma methodologies to improve productivity. Pande *et al* (2000) explained the importance of project selection and suggested that good project selection itself is a process and the potential benefits of the Six Sigma can be improved substantially if project selection is good.

Often project selections involve evaluation of individual projects and make a decision so that the objectives of the organisation will be achieved. But there is big difference between a typical R&D project and a Six Sigma project. R& D projects may take longer time to complete and the objective of the project could change in the project time line. But Six Sigma project focus on results in a shorter time of project execution. It is also reported that the number of tools available for the selection of six sigma projects are very limited (Su and Chou, 2008) and currently in many industries, selection and prioritization of projects are purely based on subjective judgements.

A two stage process for the selection of projects in an organisation was explained by Padhy and Sahu (2011). Figure 6.2 is the proposed method for project portfolio selection. The first step involves risk assessment of projects and the calculation of real value of the project. The second step involves considering several Six Sigma project for funding depends on the project value. Once the lists of projects are

selected, those Six Sigma projects can be classified into one of the following categories.

- Customer Satisfaction
- Productivity improvement/waste minimisation
- Cost Reduction
- Quality improvement
- Process improvement
- Reliability improvement
- Health, Safety and Environment (HSE)

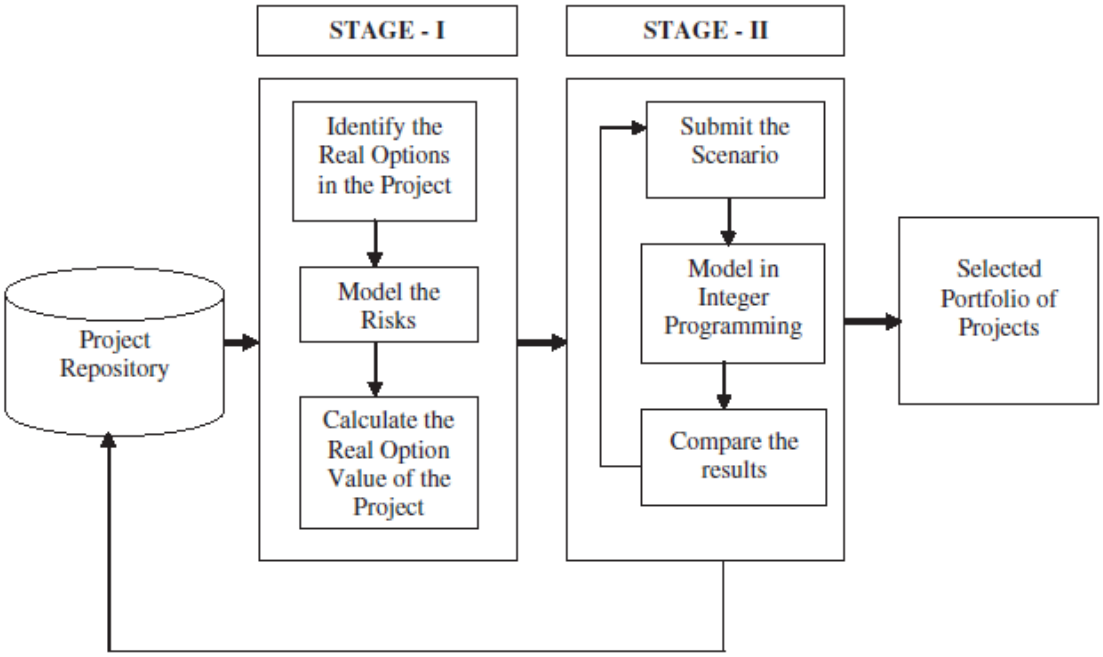


Figure 7.2: Two stage method for project portfolio selection {Adapted from Padhy and Sahu, 2011}

7.2.2. IMPLEMENTATION OF SIX SIGMA

Numerous articles have been published on the challenges and the realities in successful implementation of Six Sigma methodologies in an organisation. According to Hoerl (2001), Six Sigma implementation in various organisations has been one of the few successful technically oriented initiatives from business leaders and financial community. Kwaka and Anbarib (2006), have published a paper on

"Benefits, Obstacles and Future of Six Sigma Approach", which has reviewed the key benefits and challenges of Six Sigma practices. This literature has also identified and discussed the key successful influential factors in Six Sigma project implementation. The two perspectives of Six Sigma process which is a) the statistical view point and b) the business view point are explained by Antony and Banuelas (2001). According to the statistical view point Six Sigma is defined as having less than 3.4 defects per million opportunities but in the business world Six Sigma is a business strategy to improve the effectiveness and efficiency of all operations to meet or exceed customer expectations and thereby improve the business profitability. Table 6.1 below shows the five key steps and processes in Six Sigma for continuous improvement.

Table 7.1: Five key steps and process in Six Sigma for continuous improvement {X6σ Consulting, 2009}

Key Steps in Six Sigma	**Processes**
DEFINE	• Define the impact of the project • What is the goal/ target to achieve • Who needs to be part of the project • What are the factors which get impacted by the project • What is the time line to finish the project
MEASURE	• Take a picture of the current state, just before making any improvements • Collect data and understand the main contributors of the issue • Calculate the current process capability to meet specification • Analyse or assess current measurement system (equipment, process and people)
	• Assess all potential causes of the problem • Identify the root cause of the problem

ANALYSE	• Conduct necessary studies, experiments to identify the key variables/factors • Fully understand the problem and identify what is required to fix it
IMPROVE	• Implement required solutions • Failure Mode Effective Analysis • Pilot/test solutions • Develop full deployment / implementation plan
CONTROL	• Sustain and gain by standardising processes • Identify the key variables/ measures that should be controlled • Develop clear procedures documenting how to do things once the project is over • Validate the changes as per internal procedures

According to Antony *et al* (2003) the fundamental principle of Six Sigma is the implementation of rigorous statistical tools and techniques in an organisation to improve the level of Sigma capability. Many companies including Pall Corporation have made investments in Six Sigma training to the employees and these investments in Six Sigma projects can be viewed as capital investment projects.

7.3. CASE STUDY- 3 [IMPROVED HEATING SYSTEM FOR NON-CONTACT WELDING OF MODULE ASSEMBLIES- SIX SIGMA PROJECT]

7.3.1. INTRODUCTION

Pall Ilfracombe uses non-contact heater plates for welding of module assemblies. Welding of filter components is a critical process in the manufacturing of filter modules. The temperature on the surface of the hot plate must be uniform otherwise cold spots can results in poor quality welds. The uneven temperature distributions on non-contact heater plates was an ongoing issue within Pall Ilfracombe and this

project was initiated to identify the root-cause of the issue and improve the throughput by reducing the number of weld rejects using Six Sigma Lean methodologies. The Six Sigma Philosophy uses data and statistical tools to systematically improve processes and sustain process improvements (Picard, 2002). The sigma (σ) rating represents the proportion of defect-free products produced in a manufacturing process, reflecting how well the process is performing and how often a defect is likely to happen. As the sigma value goes up, the less variation and fewer defects the process will have. Six Sigma is a project-focused approach consists of five different phases: Define Measure, Analyse, Improve and Control (DMAIC) as shown in table 7.1. Each project must complete the five phases in chronological order.

7.3.2. DEFINE PHASE / PROJECT DESCRIPTION

All Six sigma projects start with a problem statement. The problem statement for this particular project was *"Uneven temperature distribution on non contact welding heater plates is an on-going issue within PILF. This needs to be studied in detail and the problem needs to be eliminated"*. The project objective was to increase the yield to ≥94% and thereby increase the throughput with a cost saving of ~ £50K/annum. Voice of the Customer (VOC) is a Six Sigma Phrase that refers to the range of results that are acceptable to a customer. Figure 7.3 explains the VOC for this project which is "Uniform temperature distribution on hot plate surface".

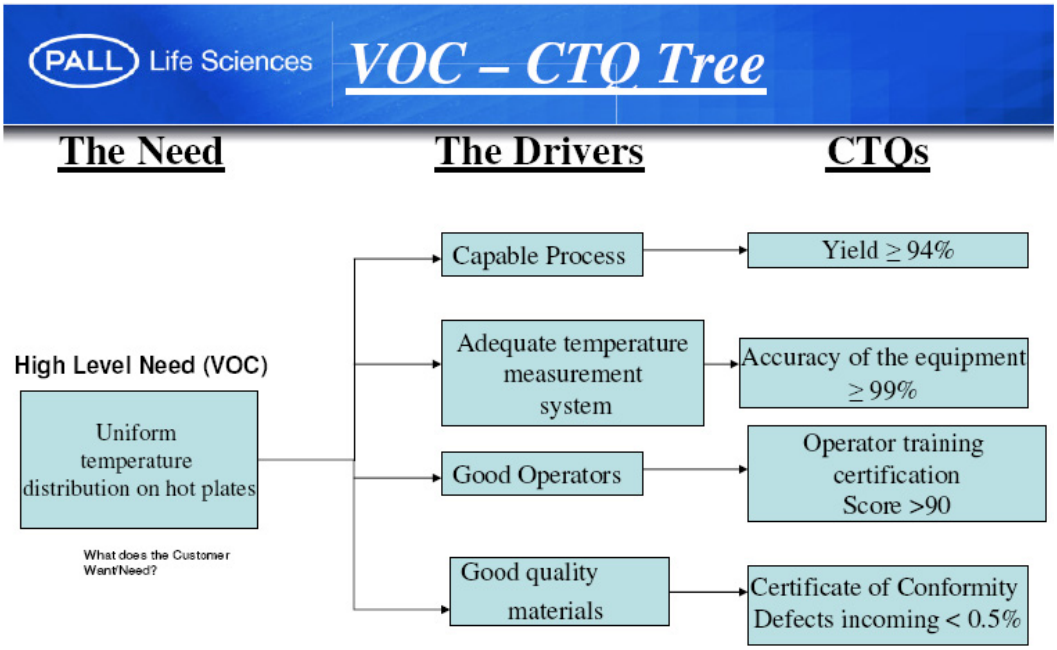


Figure- 7.3 Voice of the customer (VOC) profile for hot plate project.

CTQ means Critical to Quality and these are quality parameters that indicates the particular need of the customer. A VOC-CTQ tree is a process to convert the need of the customer to few key parameters which are critical to the quality outputs.

7.3.3. MEASURE PHASE

This phase of the project mainly determines the current performance and the target performance of the process. Figure 7.4 is a Q diagram which shows the list of questions asked to find "how the temperature on the surface of the hot plate is measured".

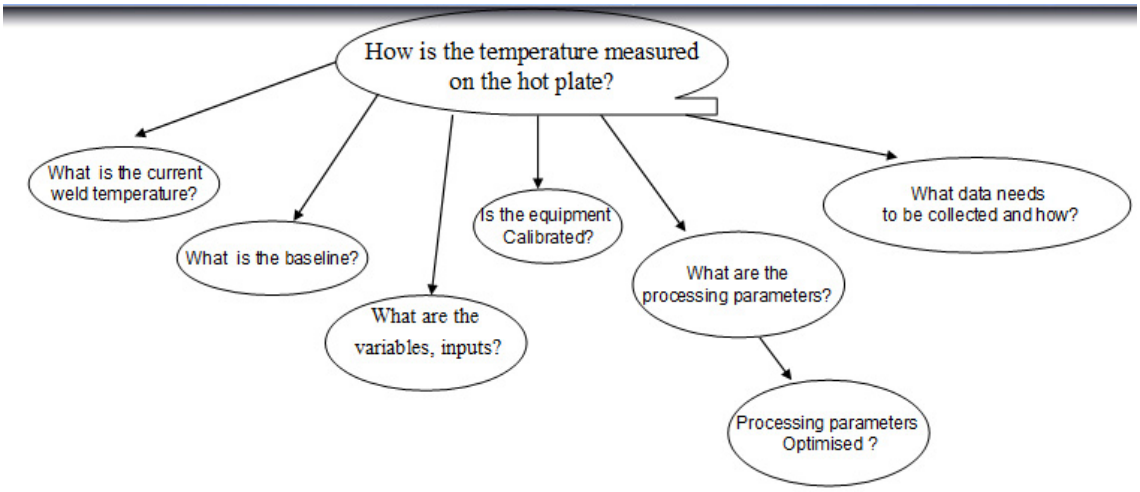


Figure 7.4 – Q diagram

I-mR chart

I-mR indicates "Individual Moving Range" and this is a valuable tool which helps to determine whether the current process is in control or not. Individual charts plot each value (Yield) as a separate point and Moving Range plots the range of two adjacent values against the number of observations. Figure 7.5 is an I-mR chart which shows yield measured for 7 months before starting the project. The average yield was 91.39% and the aim of this project was to increase the yield to ≥ 94%.

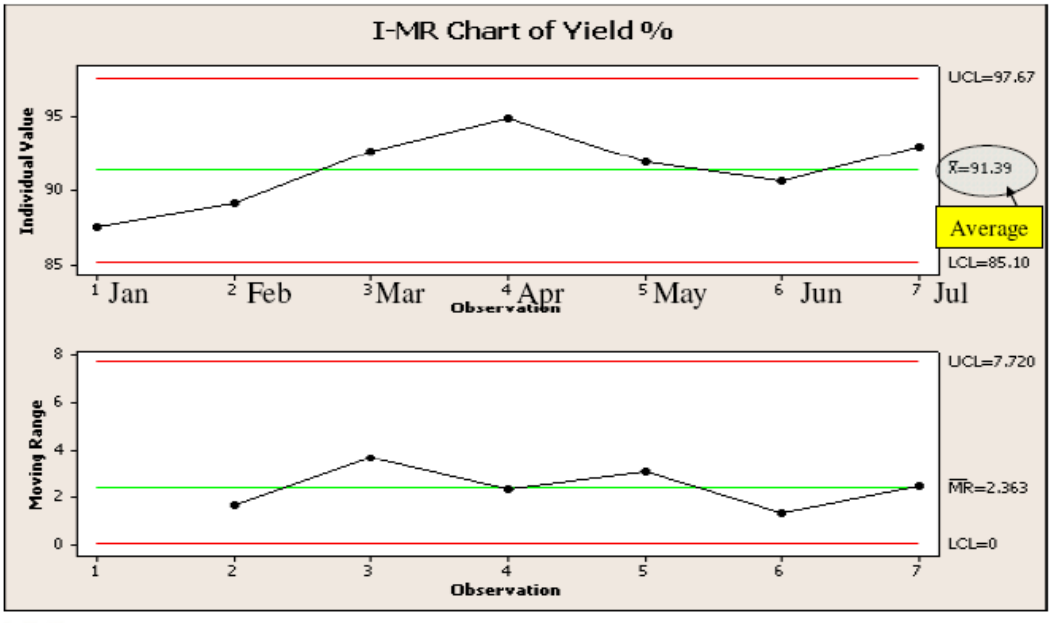


Figure 7.5: Yield measured for seven months before starting the project

Box Plot

The box plot is a graphical representation of the mean or median of a set of data. Figure 7.6 shows the non-uniform distribution of temperature on both sides of a hotplate at four points, including Top (T), Bottom (B), Left (L) and Right (R).

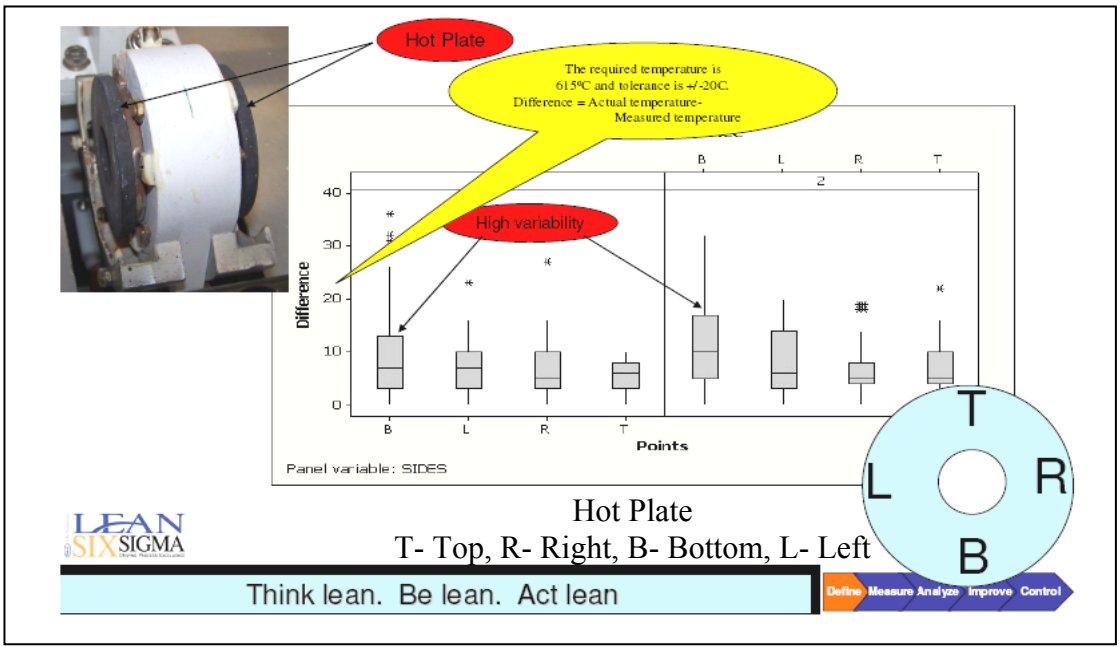


Figure 7.6: Box plot illustrating the non-uniform temperature distribution on the hot plate surface.

Pareto Chart

A Pareto chart is a graphical representation of the magnitude of the problems that offer the greatest potential for improvement. This chart displays the importance of the problem in a simple visual format and also helps a team to focus on the causes of the problem that will have greatest impact if solved. Figure 7.7 shows a Pareto chart of weld rejects occurred in three different shifts A, B and C. The graph shows the frequency of defects is almost same on each shift. Figure 7.8 is a Pareto chart of weld rejects from three different welding machines. The chart clearly shows 50% of the weld rejects were happened on PW 7 machine, 30% weld rejection happened on filter modules welded on PW 8 machine and remaining 20% of weld rejects were happened on PW 5 welding machine.

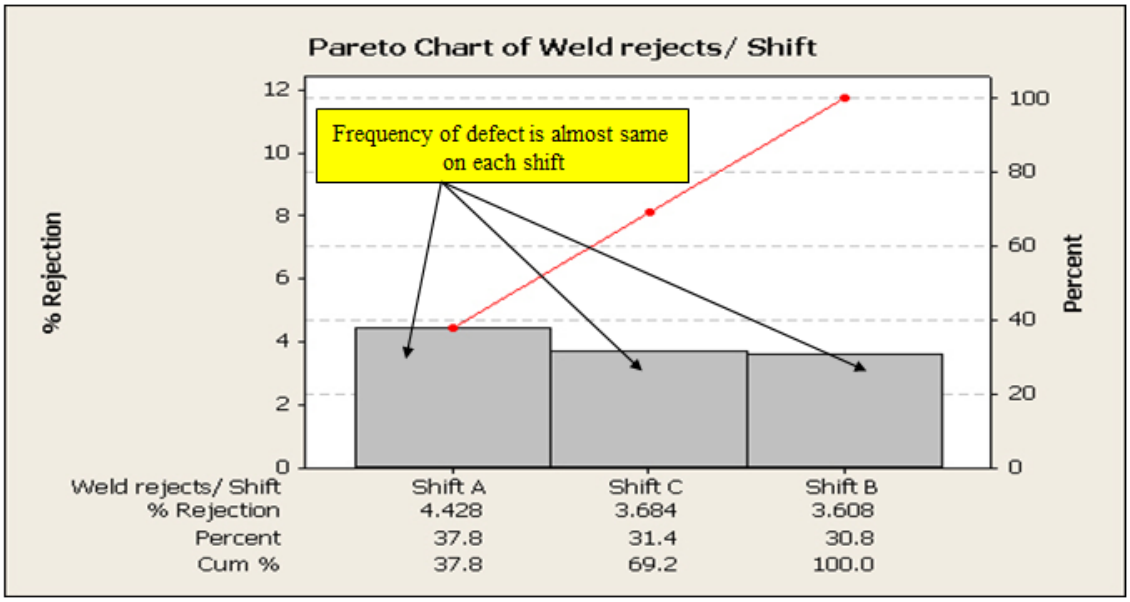


Figure 7.7: Pareto chart of weld rejects from three different shifts

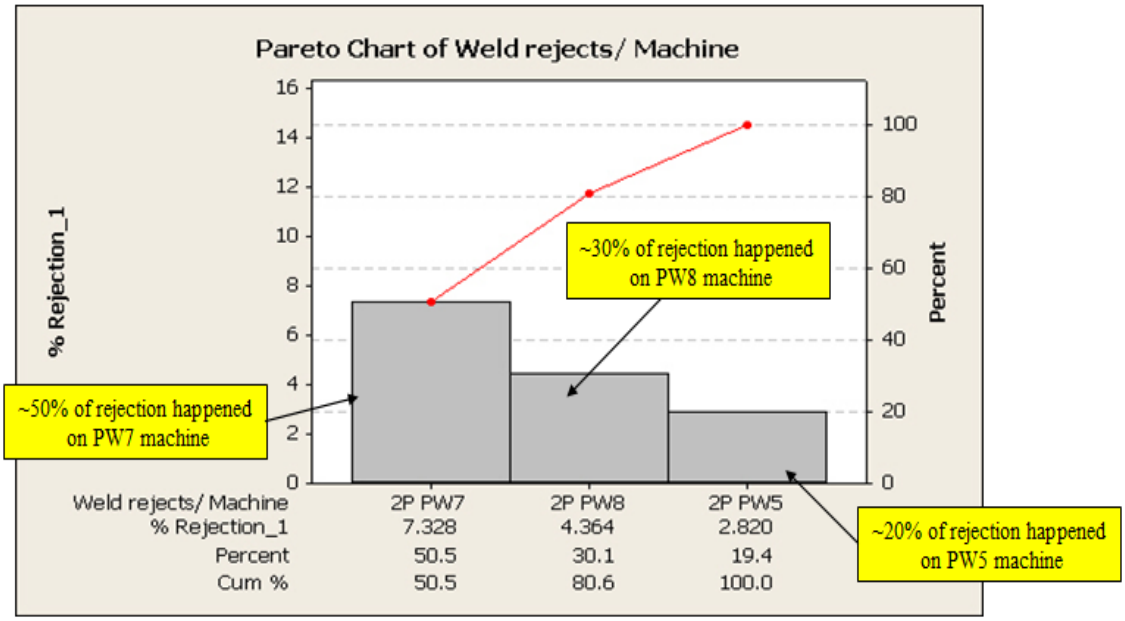


Figure 7.8: Pareto chart of weld rejects from three different machines

7.3.4. ANALYSE PHASE

Analyse phase uses data to identify critical features of a good product and establish the key process inputs that causes the defects.

Root cause analysis

A fishbone diagram or a cause & effect diagram graphically displays the most likely causes related to the problem. This tool helps to focus on the content of the problem and helps to focus on the causes, not symptoms. Fishbone diagrams are effective tools to help facilitate brainstorming sessions. Figure 7.9 is the output of a brainstorming session on the causes of uneven temperature distribution on both sides of a hot plate. After a detailed investigation it was found that the problem was related to the non-alignment of temperature between product specification temperature, machine set temperature and actual temperature on the hot plate.

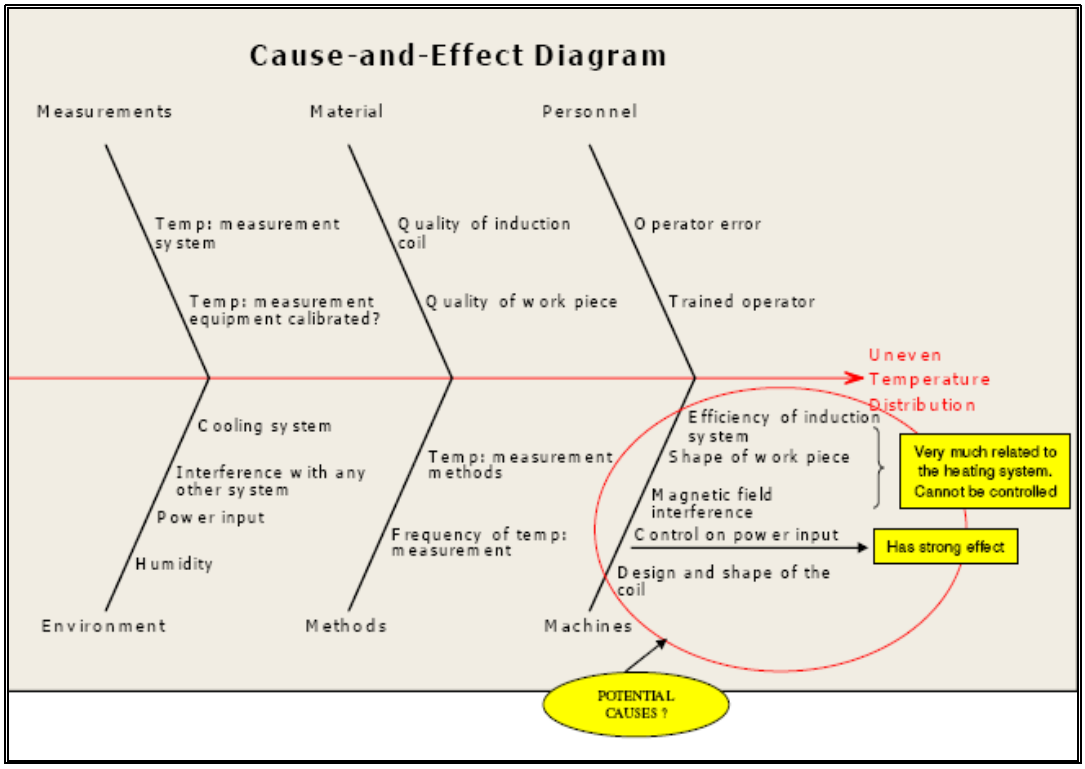


Figure 7.9: Fishbone diagram for evaluating uneven temperature distribution.

Root cause analysis has showed potential causes for uneven temperature distribution on the hot plate surface were due to the following reasons

- Efficiency of induction system- Heat generation capacity of the induction heating system

- Shape of work piece- Shape and holding of the work piece determines the gap between the hot plate and part surface
- Magnetic field interference- Magnetic interference can change the efficiency of the heating system
- Control on power input- Poor control on power input can create temperature mismatch between set temperature on the machine and actual temperature on the hot plate surface
- Design and shape of the coil- Induction coil should be designed based on the geometry of the weld surface.

Detailed investigation has showed there was a mismatch between the set temperature on the machine and actual temperature on the hot plate on the PW 7 machine. Temperature data was collected for three months from the PW 7 machine and plotted using an I-mR chart (figure: 7.10). The machine set temperature was 610° C and the average actual temperature on the hot plate surface was 632°C.

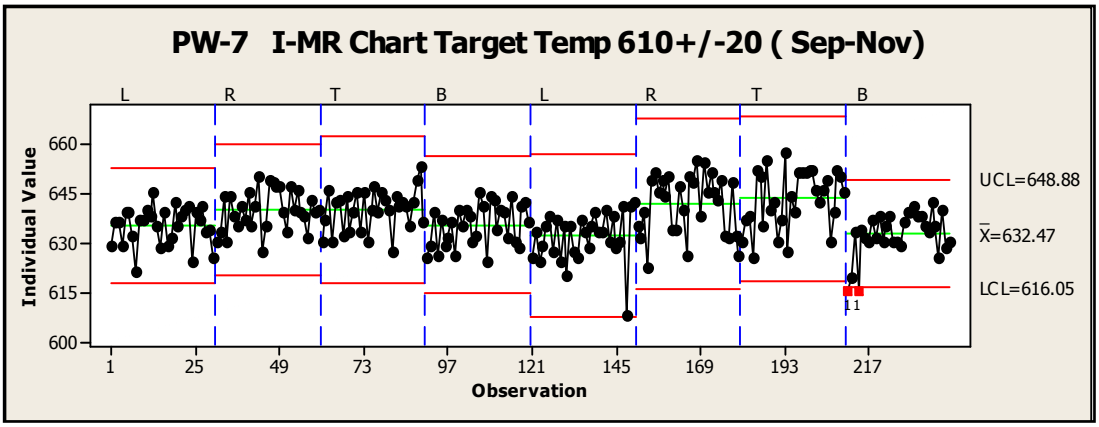


Figure 7.10: I-mR chart of four months temperature data collected from PW 7 machine

Higher temperature on the hot plate can cause higher weld failure rate and this could be due to the following reasons:

a) Gap gauge failure- The distance between the two welded parts is outside the specification limit. Higher temperature on the hot plate creates more melt at the weld interface and reduces the gap between the welded parts.

b) Banana effect- Due to higher temperature on the hot plate, un-even melting occurs at the weld interface and forms distorted weld joints.
c) Scorching effect- Higher temperature at the weld interface can degrade the polymer and forms weaker weld joints.
d) Internal flashing- Higher temperature creates more melt at the weld interface and forms internal flash during the welding process.

Figure 7.11 shows the temperature mismatch on the non-contact welder before the machine modification.

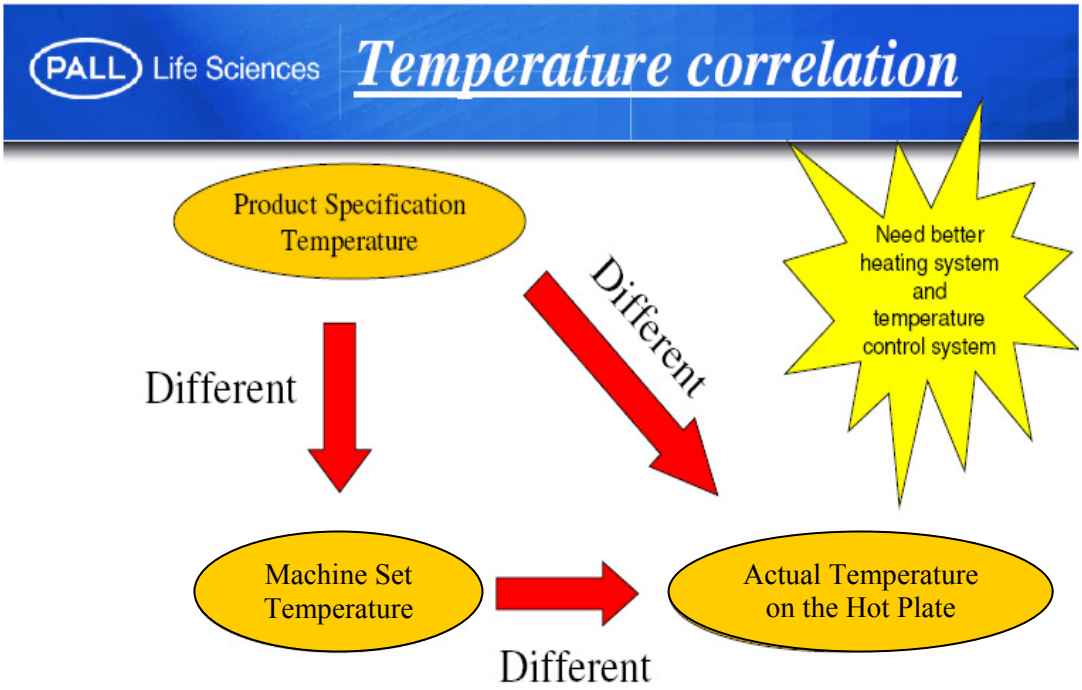


Figure 7.11: Temperature correlation before machine modification.

7.3.5. IMPROVE PHASE

The improve phase implements different methods to improve and optimise the outputs and reduce / eliminate waste. The heating system was fully modified and a Design of Experiment (DOE) was performed to optimise the processing parameters. Product specification temperature, machine set temperature and the temperature on

the hotplate surface was aligned as part of machine modification. Figure 7.12 shows temperature synchronisation after modification of the machine.

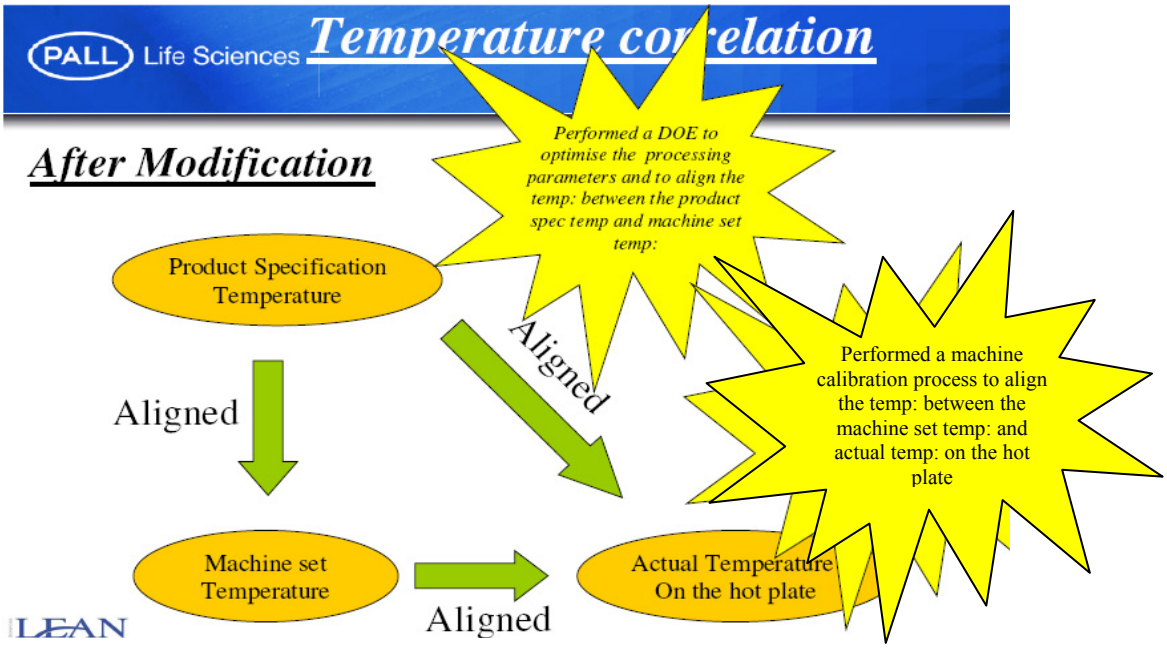


Figure 7.12: Temperature synchronisation after machine modification

Yield has been measured after the machine modification. The new yield is 96.76% compared to 91.39% before the machine modification. Figure 7.13 shows the I-mR chart of yield before and after the machine modification.

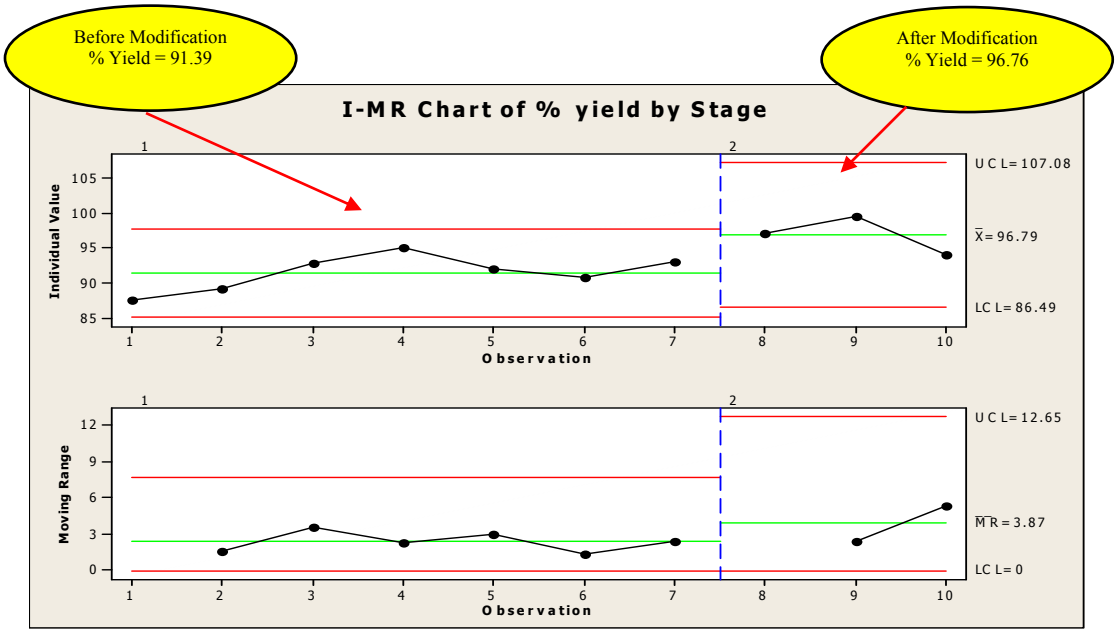


Figure 7.13: I-mR chart of Yield before and after machine modification.

7.3.6. CONTROL PHASE

The control phase aims to ensure that the implemented solution has been properly embedded into the process so that the quality will be sustained even after the project has been closed (X-Six Sigma consulting, 2009). Regular calibration procedures were implemented within the welding unit to obtain temperature reading uniformity between heater plates and temperature controller.

7.4. CHAPTER SUMMARY

The Six Sigma methodology is a project focused approach mainly consists of five different phases, Define, Measure, Analyse, Improve and Control. This chapter has covered different process involved in the five different phases of Six Sigma. A Six Sigma project has been completed as part of the process excellence program at Pall Ilfracombe. With this project, a temperature non-uniformity problem on a non-contact welding machine has been investigated in detail and a solution has been found. After the machine modification the yield has been increased from 91.39% to 96.76%. Process improvements were achieved by implementing Six Sigma methodologies in a manufacturing environment at Pall Ilfracombe.

CHAPTER 8. FINAL DISCUSSION AND CONCLUSIONS

Pall Corporation is a materials science and engineering company with the broadest filtration separation and purification capabilities in the world. Pall Ilfracombe is a manufacturing site supplying industrial and pharmaceutical filters to Pall Europe. Pall's UK manufacturing costs are increasing faster than other manufacturing sites around the world so new strategies and the implementation of new technologies are required for a step change in competitiveness. The Knowledge Transfer Partnership has successfully introduced expertise in new materials technology and improved techniques for the evaluation, quality assessment and final approval of manufactured products.

Filtration is the process of removing solid particles from a liquid or gas by passing it through a permeable medium. Various filtration mechanisms were briefly explained in chapter two of this report. The majority of Pall products are thermoplastic based and a process flow has been briefly explained (figure 2.8). Polymeric components (except the media and drainage layer) are injection moulded and Pall sub-contracts the manufacture of most of the injection moulded parts. Endcapping is a key process within filter manufacturing and various steps involved in this process have been briefly explained in chapter 2 of this report.

The aim of the thesis was to develop a strategy for process improvements in manufacturing polymeric filters at Pall Ilfracombe. To achieve the aim, five objectives were developed and have been fully met. These objectives and how they have been met are summarised in Table 8.1 and discussed in detail in this section.

Table 8.1: Five objectives and how the objectives have been met

Objectives	***How the objectives have been met***
Transfer polymeric materials knowledge to the company for the development of new products through effective materials selection and quality evaluation	Following recommendations were made a) Importance of setting up an in-house materials characterisation facility for quality assessment. b) Use of analytical techniques to assess the quality of the raw materials and filter components. c) Establishment of quality control methods within the factory and external suppliers for better quality control in polymer production process.
Set up a materials characterisation facility at Pall Ilfracombe to assure the quality of plastic parts used to manufacture filter modules	A new materials characterisation laboratory facility was established within Pall Ilfracombe for the quality assurance of raw materials and moulded parts for the manufacture of filtration systems.
Provide, via onsite materials characterisation, a better understanding of the materials and creates a general awareness of material's physical, chemical and thermal behaviour.	Polymer characterisation techniques were applied within Pall Ilfracombe for the selection and quality assessment of materials to manufacture best quality filter systems. Several case studies including identification of batch to batch variation in polymer feed stock, investigation of contamination issues and welding / endcapping issues were explained with relevant examples in chapter 5 of this thesis.
Evaluate production line issues and through the understanding of the materials chemistry to optimise processing parameters.	Pall Ilfracombe has introduced procedures for quality control of thermoplastics for industrial filters using identiPol QA thermo-mechanical analysis. A benchmark has been created for each grade of polymer and a QC procedure has been established on the premises of three suppliers who manufacture moulded components for Pall Ilfracombe.
Implement and demonstrate Six Sigma process improvement approaches for quality control of materials.	A Six Sigma project has been completed as part of the process excellence program at Pall Ilfracombe. Process improvements were achieved by implementing Six Sigma methodologies in a manufacturing environment at Pall Ilfracombe.

Chapter 3 covered a detailed literature review on various quality related issues and their potential causes in a polymer processing environment. This chapter covered the thermal degradation mechanisms in polyolefins and polyesters and the importance of implementing quality control methods in a plastic processing industry to achieve desirable end user properties. Degradation mechanisms of virgin and recycled polymers are different and the applications where recycled polymers cannot be used for making products were discussed in this chapter. Contamination of polymers with a variety of polymer additives such as pigments can cause the rejection of a whole batch of filter components. Chapter 3 also discussed the importance of implementing various cleaning procedures within external filter component suppliers to avoid contamination issues during processing. The following methods were discussed and recommended to tackle the process related quality issues at Pall Europe

a) Importance of setting up an in-house materials characterisation facility for quality assessment.
b) Use of analytical techniques to assess the quality of the raw materials and filter components.
c) Establishment of quality control methods within the factory and external suppliers for better quality control in polymer production process.

Before starting this KTP project, the levels of product non-conformance due to materials problems at Pall Ilfracome had added costs and there were only limited materials expertise within the company to solve the problems. This project has transferred materials knowledge to the company and implemented a quality control procedure to eliminate or reduce batch to batch variability within polymer feedstock.

Pall Ilfracome needed to develop more in-house materials testing knowledge and develop a strategy to setup a characterisation facility to permit effective and timely quality control checks at point of manufacture. Chapter 4 explained the knowledge and materials expertise transferred to Pall Ilfracombe through the knowledge transfer partnership with University of Bath which has resulted in the purchase of polymer analysis equipment. The creation of a polymer matrix for identification of all Pall thermoplastics and the establishment of in-house materials characterisation

facility has allowed accurate characterisation of engineering polymers used in the filtration industry. A benchmark for each raw material and moulded parts has been established and tightening of materials specification has been achieved resulting in smooth production runs. Chapter 4 explained the different techniques for polymer characterisation. Which of these techniques are appropriate in any given case is dictated by the need of the user. Many commercial polymers not only contain the base material but also a range of performance enhancing additives such as antioxidants, stabilisers, plasticizers, fillers etc. Consequently characterisation of such chemicals can be extremely complicated. A variety of thermal and chemical characterisation methods are available and the most powerful methods which are relevant to this project are explained in chapter 4. Figure 8.1 shows pictures of different characterisation equipment purchased as part of setting up an advanced materials characterisation facility at Pall Ilfracombe

Figure 8.1. Advanced materials characterisation equipment installed at Pall Ilfracombe

Establishment of an advanced materials characterisation facility was one of the key objectives of this thesis and one of the many achievements with this KTP program.

Several case studies including identification of batch to batch variation in polymer feed stock, investigation on contamination issues, welding / endcapping issues were explained with relevant examples in chapter 5 of this thesis. Pall Ilfracombe has already benefited from its capability to characterise polymeric materials and assessment of materials related manufacturing issues.

Before this KTP project there was a lack of ability to profile materials for process set-up and the smooth running of various filter manufacturing units within Pall Ilfracombe. Chapter 6 has described the implementation of a quality control procedure as part of transferring materials technology expertise to Pall Ilfracombe. This chapter explains the introduction of a method for quality control of thermoplastics for industrial filters using an identiPol-QA thermo-mechanical analyser within Pall Ilfracombe. This chapter also covered a detailed literature review on identiPol-QA and its functionalities. A bench mark has been created for each grade of polymers and a QC procedure was established at three suppliers who manufacture moulded components for Pall Ilfracombe. By implementing this QC procedure, Pall Ilfracombe is not concerned about the performance of production machinery which was previously variable depending on the base polymeric material being processed. There is a potential chance for a roll out program to introduce this QC procedure across all manufacturing units of Pall globally.

A poster was presented at the Antec2010 conference in Orlando, USA with a title "Quality control of thermoplastics for industrial filters using the identiPol-QA thermo-mechanical analyser" (Appendix 1). For polymeric product manufacturing industries quality control of plastic moulded parts is a prime requirement in preparation for final product assembly and maximising the production efficiency is a very challenging process. The thermo mechanical characteristics of moulded plastic parts were assessed and characterised using identiPol-QA thermo-mechanical analyser on a Pall Corporation production line. The identiPol-QA unit is a novel

plastic quality assurance testing device which generates a rapid thermo-mechanical profile of the material. Thermo-mechanical degradation during polymer processing, contamination of the moulded parts and batch to batch variation of polymers can change the flow properties of the polymers, results in processing difficulties during the final assembly process. The identiPol-QA thermo-mechanical analyser has proved to be a suitable technique for the quality assessment of polymers providing clear values of the glass transition temperature (Tg), Melting point (Tm), tan delta and Quality Index Score (QIS). The benefits of the identiPol-QA analyser included:

a) A fast check on the quality of raw materials/moulded parts for identification
b) Quick, traceable quality assurance
c) Reduction in the risk of poor processing and
d) Advance warning of the need to change processing conditions.

The description of a control system for identifying batch to batch variation of polymers in an industrial environment was the main focus of the Antec2010 poster presentation.

Chapter 7 of this report explains the Six Sigma methodology for making manufacturing process improvements within Pall Ilfracombe. This chapter began with a review of studies related to Six Sigma and its key principles. A Six Sigma project has been completed as part of the process excellence program. Temperature non-uniformity problems on a non-contact welding machine have been investigated in detail and a solution found. After machine modification the yield has been increased from 91.39% to 96.76% on a non-contact platen welder. Process improvements were achieved by implementing Six Sigma methodologies in a manufacturing environment at Pall Ilfracombe.

This knowledge transfer partnership program of work constituted a series of projects for better control of materials processing, improvement in production performance

and best use of materials for new product developments. Following are the key actions undertaken within the KTP program:

a) Assessed the level of materials related problems that were encountered across the whole Ilfracombe site
b) Developed full materials specifications for polymers used by Pall Europe Ltd and created a polymer matrix for identification of all Pall thermoplastics.
c) Established a laboratory facility at Pall Ilfracombe for polymer characterisation.
d) Evaluated several production line problems related to filter products and materials
e) Evaluated production line problems related to production equipment.
f) Implemented a QC procedure for quality control of thermoplastics for industrial filters using an identiPol-QA thermo-mechanical analyser within Pall Ilfracombe.
g) Shared materials expertise to new product development team and evaluated new product materials to next generation filter products.
h) Completed a Six Sigma project as part of the process excellence program which generated a cost saving of ~ $50K by improving the yield on a non-contact platen welder.

The total commercial impacts of this KTP program to Pall Ilfracombe was a direct saving of ~ 2% quality improvement and had generated ~ $1m cost saving within the life science business unit.

CHAPTER 9. FUTURE WORK

Various quality problems related to materials have been investigated to reduce the number of rejected filter parts within the factory. The newly established materials characterisation facility at Pall Ilfracombe has been used to study the root cause of quality problems in the filter manufacturing process. Pall Ilfracombe has two new strategic opportunities for further improving competitiveness which are a) better control of material processing and b) best use of materials used in new products (KTP, 2009). The following future opportunities are identified for better process improvements in polymer filter manufacturing.

Better control of materials processing - The level of product non-conformance due to materials problems adds significantly to costs but current manufacturing knowledge on site provides only limited capacity to solve the problems. It is essential to improve the quality and understanding of incoming components creating an opportunity to target processes that are critical to optimum quality and reduction of scrap across all product ranges at the Ilfracombe plant. The future work should include an enhanced literature review which will examine quality variation and defects in polymers which result in failure of filter components. The microstructure, contamination and failure topography of filter components should be examined by Scanning Electron Microscopy in order to troubleshoot filter media related production problems.

Best use of materials for new products - Selecting the right material for the right application is essential to deliver more customised product variants to accurately match customer needs. Additional materials knowledge and new product introduction will greatly enhance the ability of Pall Ilfracombe to maintain a flow of higher value products. Future work includes working with the product development group to select the correct polymers for new applications based on polymer characterisation in the context of production.

Introduction of IR heating – The implementation of IR heating for better processibility of filter modules is in progress and process optimisation and product qualification should be completed. The existing induction based hot plates and associated controls should be removed from the welding machines and replaced with IR lamps. Production benefits of fitting IR heaters to the existing non-contact linear platen welder are:

- Quality improvements because of no contamination of the product by the heaters – the IR heaters are always well away from the product (typically 30mm) and so no contamination is possible.
- Less operator work – no contact with the product means no product residue on the heaters and so no cleaning of heaters.
- Easy control of heating – heating effect can be controlled by both power level and heating time.
- Differential heating – two opposing faces of a product can be heated differently by two separately controlled IR lamps.
- Instant heating available at start-up with no machine "warm up" delays.
- Energy savings - IR energy is only switched on during the welding cycle, during the remainder of the machine operation the heaters are switched off or at standby power.
- Heat when needed and where needed - IR systems only generate heat when required and concentrate it where needed and so improve operator working conditions and reduce the cooling load on clean room air conditioning units.
- Reduced cycle times - heat output from the IR emitters is highly concentrated thereby reducing cycle times compared to hot plate heaters.
- Deep melt penetrations can be achieved quickly- typically 1.5-2mm penetration within 25 seconds in polypropylene.
- Maintenance free – no regular maintenance is required.

Future work includes the implementation of IR heating on the production line supported by thermal analysis data and Six Sigma analysis.

Quality control of polymer feedstock – Future work includes the introduction of a quality control procedure within the goods-in department at Pall Ilfracombe to assess the acceptability of incoming moulded parts, the raw materials for which have been quality assured by thermal analysis at external suppliers. This approach reduces the cost born by the site due to the rejection of filters because of materials variability. Introduction of more accurate materials testing reduces the material's variability and solves specific quality issues.

Process optimization - considerable cost savings can be made by optimising processing parameters (time, temperature and pressure) for the whole product range within Pall Ilfracombe. Future work should be done for the benchmarking of polymers and the use of materials benchmarks to optimise and simplify manufacturing parameters. The provision of an enhanced on-site materials characterisation facility and better understanding of materials in general provides a solid foundation for the introduction of new products to Pall Ilfracombe.

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Quality control of thermoplastics for industrial filters using the identiPol thermo-mechanical analyser

Sreeni Kurup - MPhil Student/ KTP Associate, Department of Mechanical Engineering, University of Bath, Bath, BA2 7AY, UK
Martin P. Ansell - Reader, Department of Mechanical Engineering, University of Bath, Bath, BA2 7AY, UK
Crispian Brailey - Director, Manufacturing Engineering , Pall Europe Ltd, Ilfracombe, Devon, EX34 8BH, UK

INTRODUCTION

➢The identiPol QA unit (Triton Technology Ltd) is a novel quality assurance testing device which generates a rapid thermo-mechanical profile of polymeric materials.

➢Thermo-mechanical degradation during polymer processing, contamination of the moulded parts and batch to batch variation of polymers can change the flow properties of the polymers, resulting in processing difficulties during final assembly.

➢The identiPol QA thermo-mechanical analyser has proved to be a suitable device for the quality assessment of polymers providing clear values of the glass transition temperature (Tg), melting point (Tm), tan delta and Quality Index Score (QIS).

➢The description of a control system for identifying batch to batch variation of polymers in an industrial environment is the main focus of this poster presentation.

identiPol QA FUNCTIONALITY

➢The identiPol QA produces a rapid thermo-mechanical profile of the material. At the end of the test the sample can be compared against typical melting point and Tg data to identify the plastic.

➢It is trained by measuring at least ten fresh samples, which then constitutes a reference set

➢Now another batch of material can be compared against this reference set . A Quality Index Score is given. 7-10 indicates the samples are very similar and acceptable, 5-7 shows similarity, but with a difference, e.g. minor contamination and below 5 shows it is quite different.

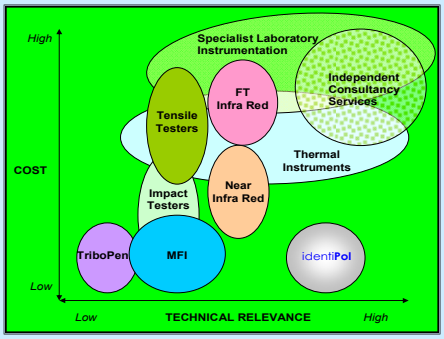

Fig.1 Positioning of identiPol in terms of cost and relevance.

Fig. 2. identiPol QA testing.

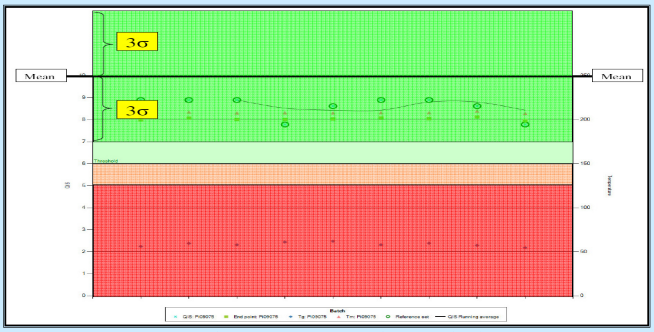

Fig. 3 6σ-based approach for the accurate identification of polymers using identiPol

RESULTS

Fig:1 Positioning of identiPol QA in terms of technical relevance and cost

Fig:2 There are two stages for running the sample. a) Moulding stage, b) Testing stage. Both are conducted sequentially by the software.

Fig:3 Chart indicates 6σ-based approach for the accurate identification of polymers using identiPol QA

RESULTS

Fig:4 Typical identiPol QA graph with data set shows results for a fairly consistent batch of Nylon 6.10 material. Tg, Tm and Quality Index Score (QIS) can be measured using IdentiPol

Fig:5 The mechanical data (similar to that gathered from a DMA (Dynamic Mechanical Analyser)) shows the Tan Delta Vs Temperature graph of polysulfone material. This graph indicates the Tg of the polymer

Fig:6 The thermal data (similar to that gathered from a DSC (Differential Scanning Calorimeter) clearly shows the melting point of PBT

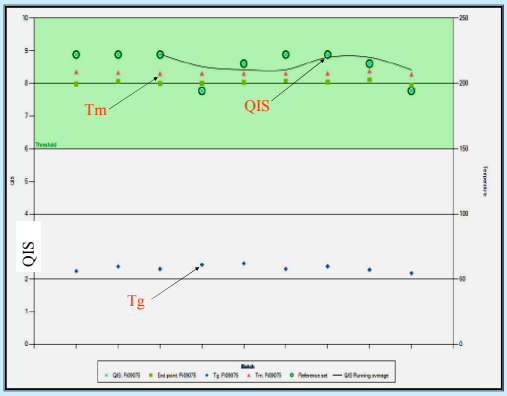

Fig. 4 QIS test results. (Nylon 6 10)

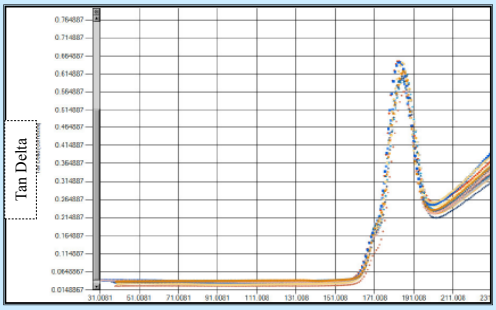

Fig. 5 Example of Tg. (Polysulfone)

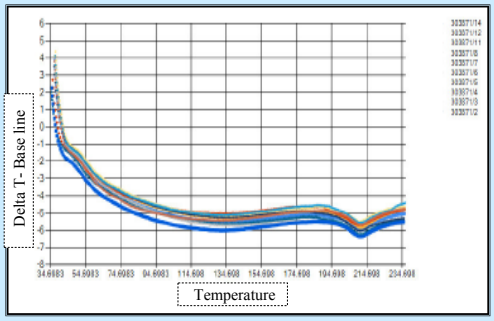

Fig. 6 Example of Tm. (PBT)

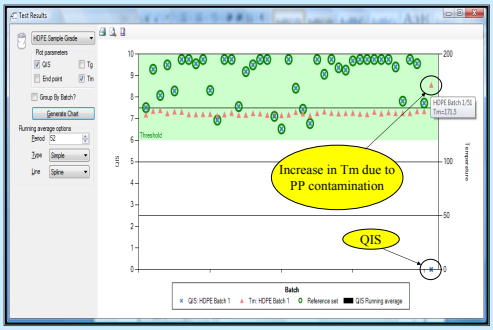

Fig. 7 Increase in detected melting point due to PP contamination

RESULTS

Fig:7 This data set shows results for a fairly consistent batch of HDPE – the final test result (small blue cross on the bottom right hand side) represents a sample of the same batch of HDPE with PP contamination deliberately introduced. The score has dropped to zero indicating significant material differences

Fig:8 The thermal data (similar to that gathered from a DSC (Differential Scanning Calorimeter)) clearly shows the presence of the polypropylene in the light blue trace (two troughs – one at around 147ºC representing the melting of HDPE and one at around 172ºC representing the melting of PP compared to a single trough in the other red, yellow and dark blue traces).

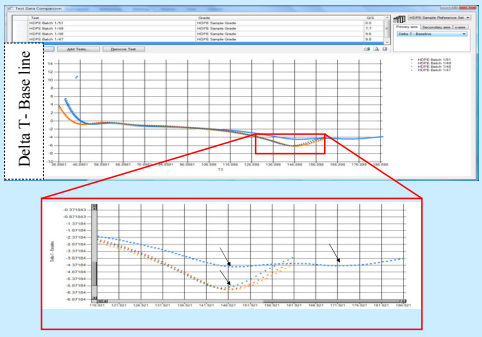

Fig. 8 Tan Delta plot (PP contamination)

CONCLUSIONS

- IdentiPol provides a method for rapid identification of polymeric materials
- Equipment allows quick, traceable Quality Assurance
- Technique reduces the risk of processing poor material
- Results warn in advance of the need to change processing conditions

SPECIFICATION

Sample size:	20-30 mg	Temperature range:	Ambient to 350 ˚C
Heating rate:	10 to 100˚C	Standard output:	Sample identification Quality Index Score (QIS) Interbatch comparison
Optional outputs:	Complex thermo-mechanical property data; tan delta, stiffness, delta T.		
Connections:	110/240V AC Universal power supply USB interface		

Sreeni Kurup: sreeni_kurup@europe.pall.com **Martin Ansell :** M.P.Ansell@bath.ac.uk

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